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Photochemistry of Some Naturally Emitted Hydrocarbons

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16. ABSTRACT

Six $C_{10}H_{16}$ monoterpenes, p-cymene, and isoprene, all known or thought to be emitted to the atmosphere by vegetation, were irradiated in the presence of NO_x. The terpenes studied included one acyclic triolefin (myrcene), two monocyclic diolefins (d-limonene, terpinolene), and three bicyclic monolefins (α-pinene, β-pinene, and Δ^3-carene). Propylene was also studied since this olefin serves as a point of reference with other chamber studies.

Results showed that monoterpenes and isoprene promoted the oxidation of NO to NO_2 and were themselves consumed at rates comparable to or greater than propylene; p-cymene was decidedly slow in these respects. The monoterpenes however did not permit the buildup of ozone due to their rapid reaction with ozone. The ozone suppression was particularly noticeable at high carbon/NO_x ratios. Propylene and isoprene were more efficient in producing ozone, but exhibited some suppression of ozone at high carbon/NO_x ratios. Para-cymene produced a uniform concentration of ozone independent of the carbon/NO_x ratio. Deciduous forests, isoprene emitters, are expected to contribute more to ozone production relative to the monoterpene producing coniferous forests. Coniferous forests may in fact function as a sink for ozone. Reported ambient concentrations of isopmne and terpenic hydrocarbons in forested areas are too low to account for more than a few ppb of ozone even if NO_x is available.

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PHOTOCHEMISTRY OF SOME NATURALLY EMITTED HYDROCARBONS

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PREFACE

Some scientists have estimated that the atmospheric loading of non-methane hydrocarbons by natural sources (i.e. emissions from vegetation and soils) is significant or even overshadows anthropogenic sources when totaled on a global basis. The emission of volatile hydrocarbons into the atmosphere is of concern since these compounds can react photochemically in the presence of oxides of nitrogen to form ozone and other oxidants. Elevated oxidant levels in the lower troposphere are undesirable since these compounds can jeopardize human health and cause damage to vegetation and materials. Although the absolute 'tons per year' estimates of natural hydrocarbon emissions and the relevance of such estimations are still very much open to question, scientists generally agree that emissions are quite high. It is therefore of interest to understand what role natural hydrocarbon emissions play in atmospheric chemistry to better assess their oxidant forming potential.

Although it is not possible to simulate exact atmospheric conditions, laboratory smog chamber experiments can provide an opportunity to study the behavior of gaseous pollutants in a controlled environment. Scientists have conducted smog chamber studies to investigate the photochemistry of diluted auto exhaust as well as the individual hydrocarbon components of auto exhaust and gasoline.

In this technical report, similar smog chamber experimental techniques were employed to characterize the photochemical behavior of volatile naturally emitted hydrocarbons. Although one cannot predict the ambient ozone burden from a quantity of naturally emitted hydrocarbons, smog chamber results can be used to compare the ozone producing ability of these compounds with that produced by anthropogenic hydrocarbons.

ABSTRACT

Six $C_{10}H_{16}$ monoterpenes, a $C_{10}H_{15}$ aromatic, and isoprene, all known or thought to be emitted to the atmosphere by vegetation, were irradiated in the presence of NO_x. The terpenes studied included one acyclic triolefin (myrcene), two monocyclic diolefins (d-limonene, terpinolene), and three bicyclic monolefins (α-pinene, β-pinene, and Δ^3-carene). The other biogenic hydrocarbons studied were p-cymene (p-isopropyl toluene) and isoprene (2-methyl-1,3-butadiene). Propylene was also studied since this olefin serves as a point of reference with other chamber studies.

Results showed that the monoterpenes and isoprene promoted the oxidation of NO to NO_2 and were themselves consumed at rates comparable to or greater than propylene; p-cymene was decidedly slow in these respects. The monoterpenes however did not permit the buildup of ozone due to their rapid reaction with ozone. The ozone suppression was particularly noticeable at high carbon/NO_x ratios. Propylene and isoprane were more efficient in producing ozone, but exhibited some suppression of ozone at high carbon/NO_x ratios. Para-cymene produced a uniform concentration of ozone independent of the carbon/NO_x ratio; this is due to its low rate of reaction with ozone. Based on this study, speculation on the photochemistry of forest airsheds is presented. Deciduous forests, isoprene emitters, are expected to contribute more to ozone production relative to the monoterpene producing coniferous forests. Coniferous forests may in fact function as a sink for ozone. Reported ambient concentrations of isoprene and terpenic hydrocarbons in forested areas are too low to account for more than a few ppb of ozone even if NO_x is available.

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SECTION 1

INTRODUCTION

Volatile hydrocarbon emissions from natural sources have recently been examined (1). Identifiable emissions can be roughly divided into two types. Type I hydrocarbons are those emitted directly from living matter. Type II are emitted as a result of the destruction of living matter. Hydrocarbons in type I, which are our main concern in this study, are the terpenoids ($C_{10}H_{16}$) and isoprene (C_5H_8) formed in green plants. Type II hydrocarbons are formed in the microbial decay of organic matter and in forest fires where large molecular weight organic molecules are broken down to lower molecular weight compounds.

Estimates of atmospheric loading of biogenic nonmethane hydrocarbons have been based exclusively on isoprene and terpenoid emission (1-3). Other sources of natural hydrocarbons, for example stress evolved ethylene (4-6) from green plants have been discounted as being too small or unimportant on the basis of background air analysis. Estimates show between 0.5 to 20 times the global atmospheric hydrocarbon emissions are due to natural sources...assuming that anthropogenic emission estimates are accurate (1,7). However ambient air analysis in suburban areas show only trace amounts of isoprene or monoterpenes. Paradoxically in rural areas where one would expect to measure greater concentrations of natural emissions, ambient air analyses show a low contribution of isoprene and monoterpenes relative to the predominate C_2-C_5 alkanes, benzene, toluene, and acetone (8). The possible explanations for this discrepancy are that the emission estimates are inaccurate for natural and/or anthropogenic hydrocarbons, or natural hydrocarbon emissions are reacting much faster than anthropogenic emissions and are removed from the atmosphere thus escaping detection.

Current field and laboratory evidence does not support the hypothesis that rural ozone is a result of natural hydrocarbons. Field studies have shown ozone and its precursors can be transported hundreds of kilometers from urban centers (9-12). The high ozone concentrations found in rural areas can be explained by the transport of anthropogenic emissions.

Despite the uncertainties associated with natural hydrocarbon emission estimates, it is of importance to examine the atmospheric chemistry of these compounds. Isoprene (2-methyl-1,3-butadiene) has been studied in the 1950's along with numerous other gasoline and auto exhaust related hydrocarbons (13). Isoprene is found in gasoline and auto exhaust at trace levels but is not a significant emission from these sources. When isoprene was irradiated with ultraviolet radiation in the presence of NO, Schuck and Doyle (13) observed moderately fast reaction rates. Isoprene reacted one-third as fast as trans-2-butene and one-fourth as fast a tetramethylethylene. Ozone was produced in the photooxidation of isoprene at a comparable concentration relative to other C_2-C_6 olefins at a carbon/NO_x ratio of 15. Using long path infrared spectroscopy several products were identified including formaldehyde, carbon monoxide, peroxyacetylnitrate (PAN), and acrolein. Glasson and Tuesday (14) classified hydrocarbon reactivity according to their ability to photooxidize NO to NO_2. They found isoprene (diolefins) photooxidized NO faster than C_1-C_4 paraffins, monoalkyl benzenes, terminal olefins, and dialkylbenzenes. Hydrocarbons which reacted faster than isoprene included the cyclohexenes, unsubstituted internal olefins, monosubstituted internal olefins, cyclopentenes, and disubstituted internal olefins.

Few studies have been reported which compare the photochemistry of the monoterpenes with the commonly studied C_1-C_{10} auto derived hydrocarbons. Stephens and Scott (15) were the first to incorporate monoterpenes in a study of hydrocarbon photochemistry. These investigators carried out irradiations at hydrocarbon and NO_2 concentrations of 5 ppm (v/v) each. The rates of hydrocarbon disappearance and formation of PAN and aldehydes were also measured. They found that the monoterpene alpha-phellandrene (p-mentha-1, 5-diene) was slightly faster than tetramethylethylene and six times faster than pinene. The isomer(s) of pinene were not specified in the study.

More recently Grimsrud, et al. (16) conducted irradiations of a number of terpenes and isobutene at 10 ppb hydrocarbon, 7 ppb NO concentration. Rates of reaction of ozone with each of the terpenes were also measured. The study showed considerable variation in hydrocarbon reactivity which depended on the number and position of double bonds in the molecule and the degree of substitution on the olefinic carbons. Darnall, et al. (17) derived rate constants for the reaction of terpenes and hydroxyl radicals from the data of Grimsrud, et al. (16). Recently a reactivity scale has been compiled for a large number of hydrocarbons based on reactivity with hydroxyl radicals (17,18). The importance of the hydrocarbon reaction rate with hydroxyl radicals in this scheme is the direct relationship of the hydrocarbon's ability to participate in chain propagating reactions leading to ozone formation. The hydroxyl radical reaction with terpenes were by far the fastest of all hydrocarbons studied.

The monoterpenes, based on past studies, can be classified as moderately reactive to very reactive (15,18). Reactivity in these studies is a measure of the rate of hydrocarbon loss during photooxidation, the rate at which nitric oxide is oxidized to nitrogen dioxide in the photooxidation of the compound, or the rate of hydroxyl radical reaction with the hydrocarbon. The effective use of hydrocarbon reactivity obtained in the laboratory to describe ambient air situations depends on the direct relationship between hydrocarbon reactivity and the photochemical oxidant potential of the hydrocarbon. Bufalini, et al. (19) recently pointed out that the relationship between reactivity and oxidant formed is probably valid if the hydrocarbon and reaction products remain in the gas phase. If a partially oxidized hydrocarbon is removed from the gas phase system by a physical process such as aerosol formation, its chain propagating behavior is essentially terminated and oxidant potential is never realized.

Many aromatics and monoterpene hydrocarbons have been found to produce large amounts of aerosols in photochemical reactions. The monoterpene hydrocarbons also produce aerosols in the dark reaction with ozone. Went (20) in 1960 first demonstrated the ability of alpha-pinene and ozone to react and form light scattering aerosols. He speculated that natural hydrocarbon emissions of alpha-pinene and other terpenes from forested areas could after reaction with ambient ozone, form the haze observed in the lushly forested areas of the Smoky Mountains of western North Carolina/eastern Tennessee.

A number of studies have demonstrated the ability of monoterpenes, mostly alpha-pinene, to form aerosols (21-30). Other investigators have also studied the aerosols formed in the dark reaction of terpenes with ozone (20, 22, 31) and when terpenes were irradiated with ultraviolet radiation in the presence of NO_x (21-30). Using infrared analyses collected terpene aerosol samples were characterized by the carbonyl ($-C = O$) stretching frequency (22-24). Laboratory samples of alpha-pinene reaction product aerosols were collected and prepared for gas chromatographic-mass spectrometric analysis using traditional acid-neutral-base extractions and derivatization techniques. Although a large number of products were present in the aerosol as evident in the total ion chromatograms, only two products were identified (26). Present in the acid fraction were pinonic acid, a cyclic keto-carboxylic acid. Pinononic acid is a homologous acid resulting from the oxidative decarboxylation of pinonic acid. Pinonic acid has also been identified in aerosol samples collected in the forested area of the Pisgah National Forest thirty miles northeast of Asheville, North Carolina (30). Unfortunately the compositional make up of the aerosol at this forested area was not determined. Had the total composition of the aerosol been identified, this information would have been of great value in determining the nature of the haze in this region of the country. More recently, however, Weiss, et al. (32) have shown that the bulk of the light scattering aerosol in the midwestern and southern United States is primarily sulfate and not carboneous. The source of the sulfur has not yet been determined.

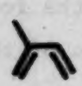
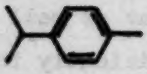
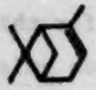
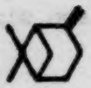
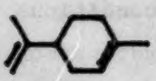
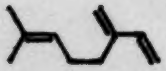
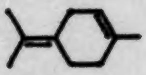
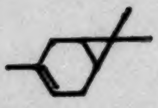
The aerosols of terpinolene and limonene formed by photooxidation in the presence of NO_x have been examined utilizing direct probe mass spectrometry (25). More than thirty products were observed which included carboxylic acids, aldehydes, alcohols, peroxides, and the nitrate esters of acids, alcohols, and peroxides.

The chemical behavior of automotive hydrocarbon emissions of C_1-C_{10} paraffins, olefins, diolefins, and aromatics in smog chamber reactions have been related to molecular structure of the compound. The naturally emitted hydrocarbons that were studied with the exception of isoprene and p-cymene are structurally unlike the automotive hydrocarbons. The naturally emitted monoterpenes are $C_{10}H_{16}$ isomers consisting of bicyclic olefins, monocyclic diolefins, and acyclic triolefins. An endocyclic olefin such as alpha-pinene easily lends itself to the formation of a dioxygenated compound through the oxidative cleavage of the double bond. The difunctional oxygenated compound which might form is likely to condense to form aerosols due to its low volatility caused by the high polar character of the molecule. The reaction with ozone as well as other chemical properties distinquish monoterpenes sufficiently from other previously studied hydrocarbons to warrant further investigations.

The hydrocarbons shown in Table 1 were chosen for this study because they were either measured in ambient air, detected as emissions from growing vegetation or found in essential oils of a number of common plants. As mentioned earlier propylene is included for comparison since it has been extensively studied in smog chambers.

This study of naturally emitted hydrocarbons was undertaken to determine the compounds photochemical reactivity, ozone-oxidant formation and reaction products under simulated atmospheric conditions. These results coupled with ambient measurements of natural hydrocarbon concentrations can be used to assess the influence natural hydrocarbon emissions have on rural and urban air chemistry.

TABLE 1. NATURAL ORGANICS: THEIR OCCURRENCE IN THE BIOSPHERE

Compound	Structure	Reason for Selection
Isoprene		Measured in ambient air in rural areas (10, 33); emitted by oak, sycamore, willow, balsam poplar, aspen, spruce, and others (3,34,35)
p-Cymene		Emitted by California black sage (36) and from 'disturbed' eucalyptus foliage (35); found in the gum terpentines of scotch pine and loblolly pine (37)
α-Pinene		Measured in ambient air in rural areas (33,38); emitted by numerous pines, firs, spruce, hemlock, cypress (3)
β-Pinene		Measured in ambient air in rural areas (39); emitted by California black sage (36); loblolly pine (40), spruce, and redwood (3)
d-Limonene		Measured in ambient rural air (39); emitted by loblolly pine (40), California black sage (39); and 'disturbed' eucalyptus (35), found in the gum terpentines of numberous pines (37) and the essential oils derived from some fruits (41,42)
Myrcene		Measured in air above pine needle litter; emitted by loblolly pine (40), California black sage (36), and redwood (3); found in the gum turpentines of some pines(37)
Terpinolene		No ambient measurements or emissions reported; however, terpinolene is found in the essential oils of numerous plants (43) and in some pine gum turpentines (37)
Δ^3-Carene		Measured in ambient air (39); found in the gum turpentines of some pines (37) and in the essential oils of numerous lower plants (43)

SECTION 2

CONCLUSION

Laboratory smog chamber investigations show the biogenic hydrocarbons isoprene and the monoterpenes are moderately to extremely 'reactive' when irradiated in the presence of oxides of nitrogen. Historically, reactivity has referred to the rate of hydrocarbon disappearance, the rate of hydroxyl radical attack on the hydrocarbon, or rate at which nitric oxide is oxidized to nitrogen dioxide; these parameters are used with the intent of providing a measure of the hydrocarbons potential to participate with nitrogen oxides and sunlight to produce ozone. This study demonstrates that the monoterpenes while reactive by these definitions are inefficient ozone precursors. This is believed to be due in large part to (1) the fast reaction of ozone with the terpenes and (2) the efficient formation of aerosol from the photooxidation products. These effects manifest themselves in a most pronounced manner at high C/NO_x ratios (50-200).

The few measurements of background ambient NO_x and detailed non-methane hydrocarbons in the literature show a wide range of values; the variations in reported values probably reflect real uncertainities in the analytical techniques and true geophysical fluctuations. Thus estimates of background NMHC/NO_x ratios exhibit a wide range assuming reported NMHC concentrations (mostly C_2-C_5 alkanes, benzene, toluene, and xylene) ranging from 40 to 100 ppbC within the United States and NO_2 concentrations on the order of 0.015 ppb to approximately 0.1 ppb. Nevertheless, this range represents conditions where monoterpenes if present would not contribute more than 1 or 2 ppb O_3 given such an NO_x poor system.

SECTION 3

RECOMMENDATIONS

It is uncertain whether the terpenes will behave at atmospheric concentrations like they behaved at higher chamber conditions. Laboratory simulations do however provide evidence for mechanisms via the products observed and thus provide a basis for atmospheric modelers to predict real world conditions. Of particular concern in this study is the relationship of aerosol formation to initial hydrocarbon concentrations. If at atmospheric concentrations terpenes are not converted to aerosols at the apparently high conversions inferred from chamber studies then it is possible that the partially oxidized terpenes will remain in the gas phase and continue to participate in photochemical processes. The end result may be that at atmospheric concentrations terpenes may be more efficiently producing ozone than is indicated at high terpene concentrations. Whether or not this is true depends in part upon the vapor pressures of the terpene oxidation products. Only fragmentary information exists about the complex composition of the terpene aerosol. However we do know that oxygenated compounds (acids, aldehydes, and ketones) in the C_{10} range are solids at room temperature and display low volatility. Furthermore recent work by other investigators has identified a number of C_2 thru C_{10} dicarboxylic acids in aerosol samples collected in the Los Angeles basin; little or none of these compounds were detected in the gas phase. It is therefore likely that the terpenes when present at ppb levels will also produce aerosol efficiently. Nevertheless there is need for cleaner reaction chambers so that irradiations may be conducted at atmospheric levels free from any wall contamination problems.

There is a need for more detailed hydrocarbon analysis of air of both coniferous and deciduous forested rural areas with accompanying ozone and accurate nitrogen oxides data. These studies would help to define the relative importance of natural and anthropogenic hydrocarbon contribution to ambient ozone. In particular the rural hardwood forested area of northeastern United States, an isoprene source area, should be examined for isoprene contribution to the non-methane hydrocarbon concentrations since isoprene has the greatest potential of the biogenic hydrocarbons for promoting ozone formation.

Another approach to assessing the impact of natural hydrocarbon emissions on ambient ozone could be a field investigation of air masses passing over sparsely inhabited forested areas. By use of aircraft equipped to collect integrated samples for hydrocarbon analysis and real time monitoring of ozone and nitrogen oxides the chemical dynamics of an air mass could be observed as it passes over forested areas. Such an experiment could be simplified by examining the hydrocarbon poor plume of a nitrogen oxides emitting fossil fuel power plant which is dispersing over a forested area. The introduction of a fresh source of nitrogen oxides to the normally nitrogen oxides poor rural air mass would allow the use of commercially available monitors which have traditionally suffered from a lack of sensitivity to low rural levels. Gaseous tracers such as SF_6 could be released concurrently at the power plant stack to follow the plume. The successful monitoring of a dispersing plume would help to provide modelers with sufficient information necessary to predict the impact of a forested area on passing air masses.

It is also recommended that any air samples collected for later terpene analysis be evaluated for loses due to reaction. In the case of whole air samples it is recommended that the ozone in the collected air be quenched immediately upon introduction to the sampling vessel and that the sample be stored in the dark to prevent photochemical reaction; the introduction of a small quantity of nitric oxide to a collection bag covered with black polyethylene has proven to be quite effective.

Lastly, it is recommended that hydrocarbon 'reactivity scales' based on rate of hydrocarbon loss, nitric oxide loss, hydroxyl radical reaction, etc. be used with some caution. Such scales have shown terpenes to be moderately to highly reactive. However, this study has demonstrated that these compounds, while promoting rapid NO oxidation, suppress ozone formation.

SECTION 4

EXPERIMENTAL

All of the hydrocarbon/NO_x photooxidation smog chamber-type experiments with the exception of those carried out in the long path infrared reaction chamber were conducted in 250 liter (2 mil) FEP Type A Teflon bags. The bags were made by heat sealing a folded sheet (18.9 cm width by 42.5 cm length) of the Teflon film using a commercial heat sealer. After two sides of the bag are sealed a two inch square of pressure sensitive tape, which helps to make an airtight seal for the inlet-outlet fitting, was placed at a suitable location on the outside bag surface. A hole punched through the tape bag surface accommodated a Teflon O-seal straight thread connector which was secured with a Teflon nut. Once the connector was in place the third side of the bag was sealed and the airtight bag was now ready for conditioning before use in experiments. Conditioning the bags was necessary because past experience had shown low levels of hydrocarbon outgassing occurred with new bags. The conditioning process involved filling the bag with 3 ppm ozone in clean air and irradiating the bag in the smog chamber for 48 hours followed by flushing with a source of clean air. A clean air source was provided by a laboratory purification train which removed water, hydrocarbons, and nitrogen oxides. Hydrocarbons were removed by combustion on a heated catalyst of rhodium on aluminum (Engelhard) and adsorption on activated carbon. Nitrogen oxides were removed by chemical absorption on Purafil (Borg Warner) and water vapor by condensation. The resulting air from the system contained less than 2 ppb nitrogen oxides and less than 50 ppb carbon as nonmethane hydrocarbons most of which were propane and ethane. To introduce a controlled amount of hydrocarbon or NO_x into the Teflon bag measured quantities of liquid or gas of the compound were injected using a calibrated syringe through a septum in a glass loop placed in-line between the air train and bag. For some of the less volatile hydrocarbons the glass loop was gently heated to assure volatization.

All hydrocarbons used in this study were of 95% or higher purity and obtained from SCM Glidden, Aldrich, or Chemical Samples Company. Nitric oxide and nitrogen dioxide were chemically pure grade obtained from Air Products.

The irradiation chamber in which the Teflon bag was suspended was an aluminum box of 0.78 m width x 1.35 m length x 1.12 m height. Two banks of 40 watt ultraviolet fluorescent lamps evenly distributed along the two inner sides of the chamber provided the necessary irradiation. In these experiments twenty two General Electric F40 BLB filtered blacklamps with energy maxima at 3660 Å and four Westinghouse sunlamps with energy maxima at 3160 Å were used to simulate lower atmospheric solar radiation between 290 and 380 nanometers. The light intensity was measured by the photolysis of NO_2 in nitrogen (44). The equation employed for this was $-d(NO_2)/dt = k_d(NO_2)$. Since $k_d = 1.5\ k_1$, this first-order dissociation constant is a measure of the light intensity. The k_d value was 0.45 min^{-1}. The irradiation chamber was equipped with an air conditioner which cooled and circulated air maintaining a temperature of 25 ± 2°C during the irradiation.

Ozonolysis experiments of isoprene and propylene were also carried out in Teflon bags thermostated at 25 ± 2°C in the irradiation chamber but in the dark. Ozone was produced by exposing purified air flowing through a high voltage discharge ozonator. At a constant air flow through the ozonator the amount of ozone produced could be varied by varying the applied voltage.

The C_2-C_3 oxygenates, propylene, isoprene, and the terpenes were analyzed by gas chromatography with flame ionization detection. Propylene, isoprene, and the oxygenates (acetone, acetaldehyde, and propionaldehyde were separated on a 46 cm x 3.2 mm diameter stainless steel column packed with 60-80 Mesh Porapak Q. The terpenes were separated on a 1.83 m X 3.2 mm diameter stainless steel column packed with 10% SF-96 on 6/80 mesh acid washed Chromosorb W. Both columns were operated isothermally at 100°C. A Perkin-Elmer model 900 gas chromatograph was modified with two solenoid actuated Seiscor gas sampling valves (Seismograph Co.). A sensitivity of 50 ppbC could be obtained on this system using a 5 cc gas sample loop.

Peroxyacetylnitrate (PAN) produced in the irradiations was measured by electron capture gas chromatograph. The system consisted of a Seiscor sampling valve with a 5 cc gas sample loop and a chromatographic column of 10% Carbowax 600 on Gas Chrom Z packed in a glass column 90 cm X 3.2 mm. A sensitivity of 0.5 ppb PAN was obtained using a wide range scandium tritide electron capture detector (Analog Technology Corporation). Both the column and detector were operated at room temperature. The system was calibrated with samples of PAN analyzed by long path infrared.

Ozone produced in the hydrocarbon photooxidation reactions or in the ozonolysis experiments was monitored with a Bendix (model 8002) instrument using the gas phase chemiluminescence of the ethylene-ozone reaction. Nitrogen oxides were measured using a Bendix (model 8101B) NO_x analyzer via the gas phase chemiluminescence of the ozone-NO reaction. Both instruments were calibrated using standard gas phase titration techniques of NO with ozone.

Wet chemical analyses techniques were also employed during the irradiation experiments. The concentration of formaldehyde produced in an irradiation of a hydrocarbon/NO_x mixture was measured using the chromotropic acid (45) method and the Saltzman (46) method used to check the NO_2 concentration against measurements made by the chemiluminescent instrument.

The ultraviolet irradiations of terpenes were also carried out in a photochemical chamber which also served as an absorption cell for in situ infrared measurements. Figure 1 is a schematic of the system. The chamber is constructed of borosilicate glass pipe (Corning QVF-PS 12-60). Six sections of pipe are connected together separated by 1.9 cm aluminum spacers with 0.32 cm Teflon gaskets on either side giving a total length of 9.1 m and an internal diameter of 0.31 m. The five aluminum spacers have inlet ports in them and were connected via a manifold to a standard gas handling system. The manifold distributes gaseous sample uniformally throughout the cell. The chamber ends were capped with 3.18 cm thick Plexiglas flat plates using Teflon gaskets. The internal volume of the chamber was 690 liter. The chamber could be evacuated to a pressure of less than 1 torr with a large displacement vacuum pump connected to one end plate with a ball vacuum valve. Samples of volatile materials or gases were mixed in known volume bulbs and introduced into the chamber through the glass manifold; terpenes low in volatility were vaporized into the gas phase by injecting liquid sample with a calibrated syringe through

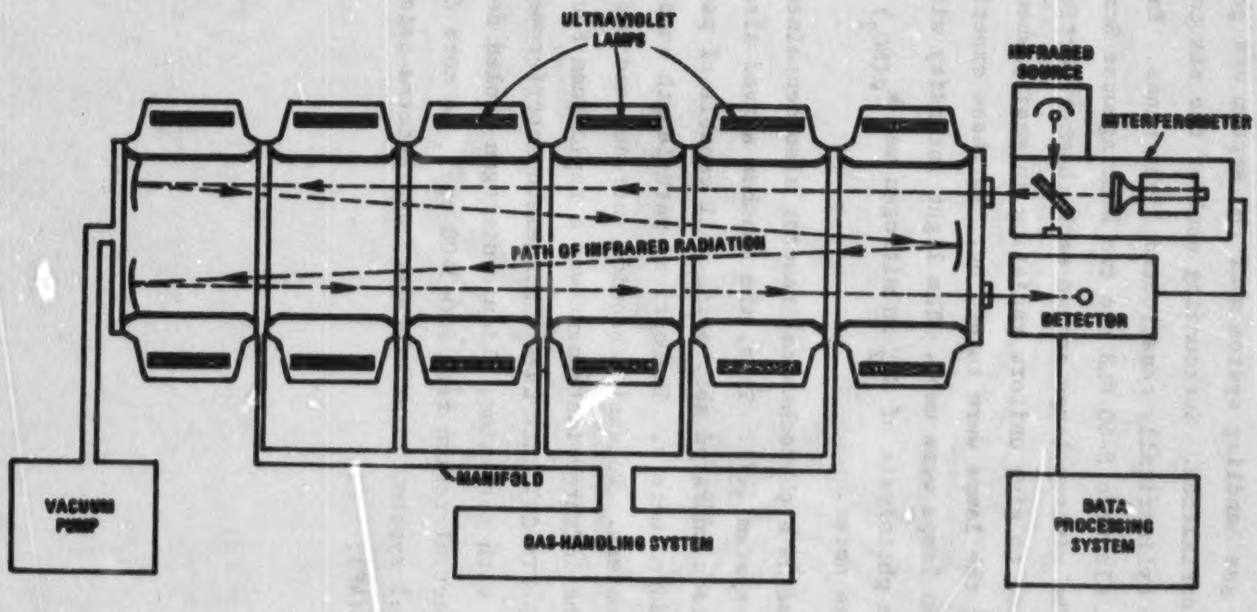

ULTRAVIOLET LAMPS
INFRARED SOURCE
INTERFEROMETER
PATH OF INFRARED RADIATION
DETECTOR
MANIFOLD
VACUUM PUMP
GAS-HANDLING SYSTEM
DATA PROCESSING SYSTEM

Figure 1. Schematic of long path infrared photochemical reaction chamber system.

a septum into a glass line on the gas handling system. The injections were made while air flowed through the gas handling system into the chamber. The immediate area of the gas handling system near the septum was gently heated to assure complete vaporization. Surrounding each of the six chamber sections were two half-section cylindrically constructed light banks. Each half section contained six General Electric F-40 BLB and two Westinghouse Sun ultraviolet fluorescent lamps. The sixteen lamps around each chamber section were arranged and controlled to give uniform radiation intensity when all, one half or one fourth of the lamps were turned on. In these experiments a total of 48 black and 24 sun lamps were used. The light intensity with these lamps on as measured by the photolysis of NO_2 in nitrogen was $k_{d(NO_2)} = 0.51\ \text{min}^{-1}$ except where otherwise noted.

This chamber used as a photochemical reactor also contained within it an eight-mirror optical system (47). Thus, the chamber served also as a long-path multiple reflection infrared absorption cell capable of path lengths in excess of several hundred meters. The optical path length used in these experiments was 357 meters. Potassium bromide entrance and exit windows were used on the cell. The infrared instrument was a rapid scan Fourier Transform Spectrometer (Digilab FTS-20) that uses a Michelson interferometer with a KBr beam splitter coated with germanium. Liquid nitrogen cooled detectors were used to cover the spectral region from 700-3400 cm^{-1}. A more detailed discussion of the optical system, interferometer, and spectra data techniques are given elsewhere (48).

SECTION 5

RESULTS AND DISCUSSION

REACTIVITY

Nine hydrocarbons were irradiated with UV radiation in the presence of NO_x and their photochemistry studied. Except for propylene all of the selected hydrocarbons are volatile compounds either identified or suspected of being emitted by vegetation. Propylene an auto exhaust related hydrocarbon was included for comparison purposes since its photochemical reactivity has been well characterized in other studies and will serve as a benchmark to gauge the reactivity of the other compounds.

Isoprene, p-cymene, alpha-pinene, d-limonene, and propylene were studied at a number of carbon to NO_x ratios (ppmC/ppm NO_x) ranging from 2 to 200 with a constant NO_x concentration of 0.33 ppm. Myrcene, terpinolene, and beta-pinene were investigated at carbon/NO_x ratios of 30 and 200 and Δ^3-carene at a ratio of 30. In an urban atmosphere C/NO_x ratios can be 6:1 during morning rush hour traffic (personal communication, W. A. Lonneman). As the urban plume ages, while being transported into suburban and rural areas, the NO_x is depleted increasing the C/NO_x ratio. In remote areas of the continental United States C/NO_x ratios are in the range 400 to 6600. The significance of these ratios with respect to the terpenes will be discussed later. The choice of experimental conditions of 2 to 200 reflects the wide range of ratios observed in the extremes of urban and remote atmospheres. The selected experiments performed at C/NO_x ratios of 30 and 200 were chosen for two distinct reasons. The ratio of 30:1 was chosen to approximate the study of Westberg (39) and represents the best case for ozone production. The ratio of 200:1 was judged as appropriate to represent a real rural/remote NO_x poor atmosphere. The results of these Teflon bag smog chamber irradiations are plotted as concentration versus time profiles in Appendix B (figures 1B-55B).

It should be noted that NO_2 concentration data acquired after the NO_2 maximum is increasingly in error with irradiation time. This error is due to the non-specificity of the heated carbon converter in the chemiluminescence monitor. Nitrogen containing species such as peroxyacetylnitrate and nitric acid have resulted in varying unpredictable conversions to nitric oxide based on converter history (49,50). Wet chemical measurements of NO_2 obtained after the chemiluminescence NO_2 peaked measured as little as 10% of the instrument response value as actually NO_2.

Smog chamber data are examined with respect to ozone producing ability as shown in Figure 2. This figure clearly illustrates and compares the varying ability of isoprene, d-limonene, alpha-pinene, p-cymene and propylene to drive the hydrocarbon-NO_x photochemical system to ozone generation. With the exception of p-cymene all the hydrocarbons exhibit maximum ozone generation at a carbon/NO_x ratio in the range of 10-20. This ratio range is in good agreement with the work of Westberg (39) who observed optimum ratios for terpinolene, d-limonene, and alpha-pinene at 25 using initial NO_x concentrations of 55 and 170 ppb. Para-cymene produces a fairly consistent 410 ppb ozone as its initial concentration is increased to give higher carbon/NO_x ratios. The effect of HC/NO_x ratio on maximum ozone can be explained by the relative contributions of ozone formation and destruction processes occuring in the photochemical mechanism. Since the photolysis of NO_2 is the only ozone forming step in the mechanism any reaction which accelerates the conversion of NO to NO_2 will ultimately increase ozone. A key step in the formation of NO_2 is the reaction of NO by alkoxy and acyl radicals formed by the hydrocarbon-OH reaction. Consequently as the hydrocarbon concentration is increased the oxidation reaction of NO to NO_2 is increased. The peaking of ozone production and the subsequent ozone decline after carbon/NO_x ratios of 10-20 are reached results from the increasing influence of the ozone-olefinic reaction. This is especially apparent at high carbon/NO_x ratios where the ranking of the compounds according to ozone production are directly related to the hydrocarbon-ozone reaction rate. Figure 3 a plot of log $k_{ozonolysis}$ versus ozone maximum at carbon/NO_x ratio of 200 shows a high correlation ($R = 0.98$) between the reaction rates with ozone and the

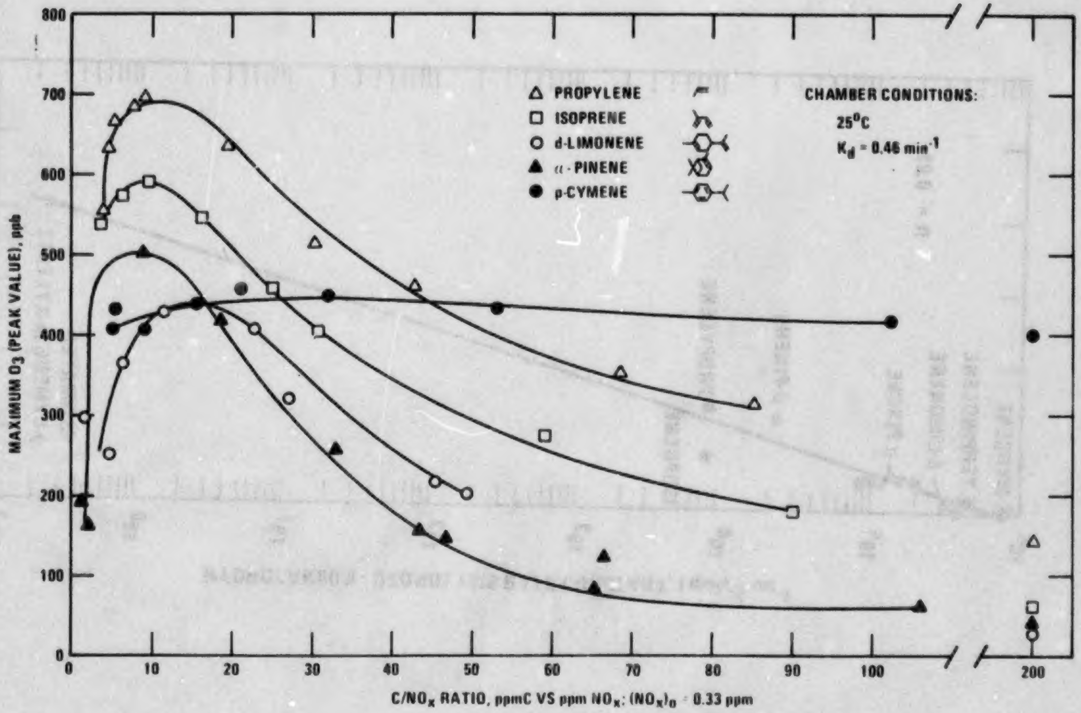


Figure 2. Effect of hydrocarbon to NO_x ratio on ozone maximum.

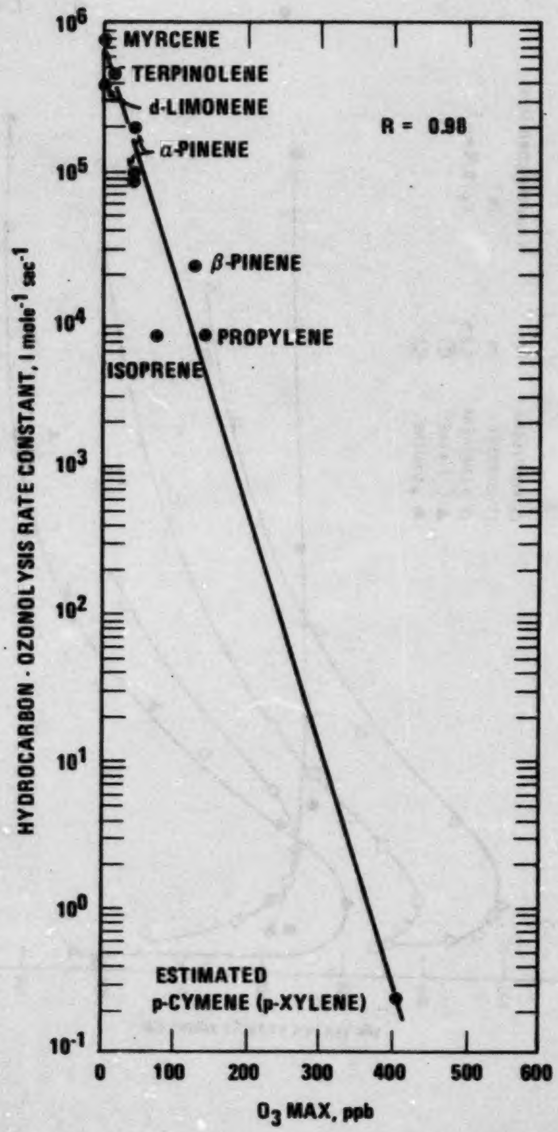


Figure 3. Hydrocarbon ozonolysis rate vs. maximum ozone. $C/NO_X = 200$; $(NO_X)_o = 0.33$ ppm.

maximum ozone formation in the photochemical reaction of these hydrocarbons. The fact that p-cymene an aromatic exhibits an apparent plateau for maximum ozone after an optimum C/NO_x ratio is consistent with its observed slow reaction rate with ozone. At carbon/NO_x ratios of 200 p-cymene reacts so slowly with ozone relative to the ozone forming process that very little ozone is depleted. In contrast, the other terpenes are reacting 10^5 to 10^6 times faster with ozone than is p-cymene (see Table 2).

Another semi-quantitative way to compare the ozone forming potential of the hydrocarbons being studied is to ratio the ozone produced to the carbon consumed at the time of maximum ozone concentration. These data are presented in a log-log format shown in Figure 4. The terpenes d-limonene and alpha-pinene at the optimum carbon/NO_x range of 10-20 are producing 1.5 to 3 ppb ozone per 20 ppb carbon consumed. Westberg (39) observed between 0.6 to 2 ppb O_3 per 20 ppbC consumed for these terpenes. Propylene and p-cymene at the same carbon/NO_x ratio produce between 2.9 to 5.2 ppb ozone per 20 ppb carbon consumed. Using the same experimental conditions at a C/NO_x ratio of 10 Dodge (51) predicted by computer modeling, an ozone maximum of 880 ppb at 150 minutes which results in the formation of 5.3 ppbO_3 per 20 ppbC consumed. The model compares favorably with the irradiation at C/NO_x of 9.0 where 700 ppb O_3 were produced at 140 minutes with the formation of 4.2 ppbO_3/20 ppbC. It should be noted that the photochemical model tends to over predict ozone concentrations by about 20-30% for most HC/NO_x systems. The reasons for this over prediction is currently under study.

Isoprene is less efficient than propylene in producing ozone on a per carbon basis yielding 2.4 to 3.5 ppbO_3/20 ppbC.

To verify if propylene and α-pinene have the same relative degree of photochemical reactivity at lower concentrations as was observed at higher concentrations, further experiments were performed. Hydrocarbon contamination from the walls of the Teflon bag used as the reaction chamber becomes significant over long irradiation periods, which necessitated a series of low concentration hydrocarbon/NO_x experiments to observe ozone produced. Table 3 summarizes the results of these low concentration irradiations. As

TABLE 2. HYDROCARBON REACTIVITY PARAMETERS AND SOME SELECTED RATE CONSTANTS

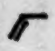
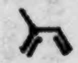
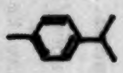
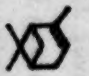
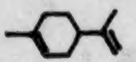
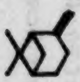
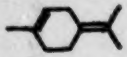
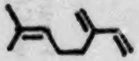
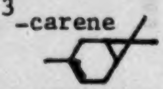
Compound	C/NO$_x$ (NO$_x$)$_o$ = 0.33 ppm	O$_3$ Maximum, ppb	Time to O$_3$ max, min.	Hydrocarbon loss, ppb min^{-1}	NO loss ppb min^{-1}	Rate Constants ℓ mol^{-1}sec^{-1}	
propylene	30	514	48	41	32	$k_{OH} = 1.5 \times 10^{10}$	a
	200	143	4	88	76	$k_O = 2.10 \times 10^9$	d
						$k_{O_3} = 7.8 \times 10^3$	g
isoprene	30	405	60	22	23	$k_{OH} = 4.7 \times 10^{10}$	c
	200	73	15	92	35	$k_{O_3} = 7.5 \times 10^3$	h
p-cymene	30	450	130	4.4	7.1	$k_{OH} = 0.92 \times 10^{10}$	c
	200	403	105	11	9.9	$k_{O_3} = 2.41 \times 10^{-1}$	i
						(p-xylene)	
α-pinene	30	260	60	32	38	$k_{OH} = 3.5 \times 10^{10}$	a
						4.7×10^{10}	c
	200	43	10	70	136	$k_O = 1.6 \times 10^{10}$	d
						$k_{O_3} = 2.0 \times 10^5$,	e
						1.0×10^5	f
						8.5×10^4	b

Table 2. (continued)

Compound	C/NO$_x$ (NO$_x$)$_o$= 0.33 ppm	O$_3$ Maximum, ppb	Time to O$_3$ max, min.	Hydrocarbon loss, ppb min^{-1}	NO loss ppb min^{-1}	Rate Constants ℓ mol^{-1} sec^{-1}	
limonene	30	309	120	39	--	k_{OH}= 9.0 X 10^{10}	a
						8.8 X 10^{10}	c
	200	3	10	111	114	k_O = 6.5 X 10^{10}	d
						k_{O_3} = 3.9 X 10^5	b
β-pinene	30	255	158	9.7	5.1	k_{OH}= 4.1 X 10^{10}	a
						4.0 X 10^{10}	c
	200	125	50	45	10	k_O = 1.5 X 10^{10}	d
						k_{O_3} = 2.2 X 10^4	b
terpinolene	30	240	100	35	40	k_{O_3} = 4.4 X 10^5	e
						6.1 X 10^6	b
	200	15	10	97	44		
myrcene	30	322	240	63	21	k_{OH}= 13.7 X 10^{10}	c
	200	1.5	10	130	36	k_{O_3} = 7.6 X 10^5	b
Δ^3-carene	30	250	70	22	8.6	k_{OH}= 5.2 X 10^{10}	c
	NA	--	--	--	--	k_{O_3} = 7.4 X 10^4	b

a Reference: 52 b Reference: 16 c Reference: 52(derived from Ref. 16) d Reference: 53

e Reference: 54 f Reference: 24 g Reference: 55 h Reference: This work. See Appendix 1

i Reference: 56

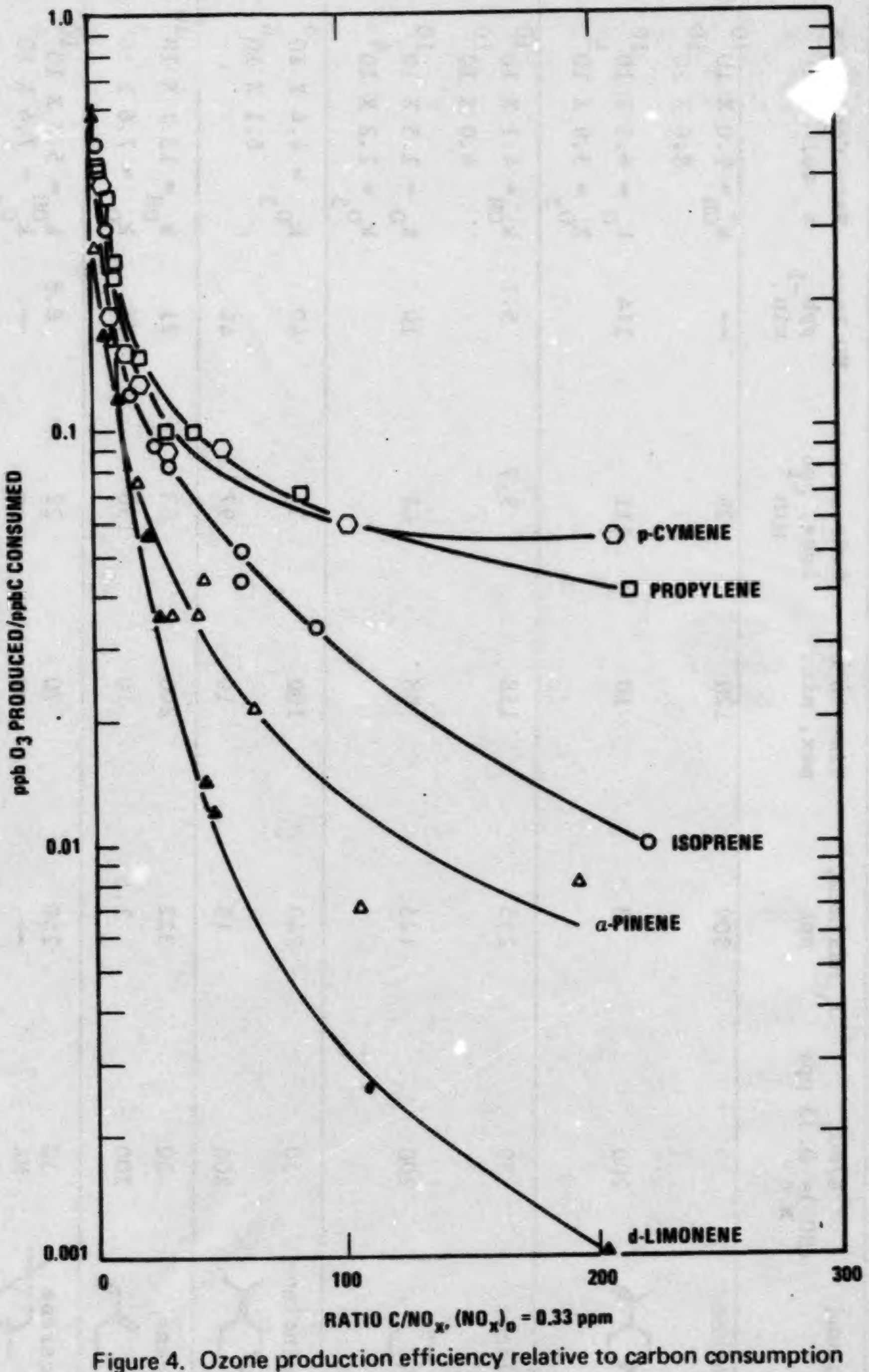


Figure 4. Ozone production efficiency relative to carbon consumption vs. C/NO_x.

observed at the higher concentrations, the propylene/NO_x system produces more ozone than the α-pinene/NO_x system under similar conditions. These sets of experiments demonstrate that doubling the C/NO_x ratio corresponds to doubling of carbon which increases the ozone production. This agrees with the higher concentration experiment where maximum ozone production occurred as the C/NO_x ratio approached 30:1.

TABLE 3. RESULTS OF IRRADIATED PROPYLENE-α-PINENE/NO_x AND NO_x SYSTEMS AT LOW CONCENTRATION

PROPYLENE

C/NO_x	$[C]_i$ ppbC	$[NO_x]_i$ ppb	$[O_3]_{60\ min}$ ppb	$[\%NO_2]_i$	$[\%NO_2]_{60\ min}$
7.5	88	11.7	29	49	85
4.6	89	19.5	23	23	50
11	97	8.7	27	48	86
16	184	11.5	37	48	88

ALPHA-PINENE

C/NO_x	$[C]_i$	$[NO_x]_i$	$[O_3]_{60min}$	$[\%NO_2]_i$	$[\%NO_2]_{60min}$
4.6	110	24.0	11	27	57
8.4	101	12.2	16	35	72
12.2	123	9.6	14	43	76
16.5	198	11.5	21	48	91

NO_x BLANK

		$[NO_x]_i$	$[O_3]_{60\ min}$	$[\%\ NO_2]_i$	$[\%NO_2]_{60min}$
--	--	9.2	6.1	35	73
--	--	10.6	5.5	29	49

Other indicators used to characterize hydrocarbon reactivity include the rate of nitric oxide oxidation or time to NO-NO_2 crossover, rate of hydrocarbon consumption and related parameters such as time to 50% hydrocarbon loss. In their reviews of photochemical air pollution Altshuller and Bufalini (57,58) found hydrocarbon reactivity based on rates of nitric oxide oxidation and hydrocarbon consumption gave similar hydrocarbon rankings. Recently Wu (59) reported that rates of hydrocarbon consumption and nitric oxide oxidation correlated to a high degree with hydrocarbon-OH rate constants.

Hydrocarbon loss rates from this study were plotted as a function of carbon/NO_x ratios and shown in Figure 5. All of the terpene compounds displayed a high degree of reactivity except for p-cymene. This is consistent with data in Figure 6 in which p-cymene reaches its ozone maximum at an irradiation time ten times longer than the other terpenes all at the same initial concentration. However, as seen in Figure 2 p-cymene produces 400 ppb or more ozone even at carbon/NO_x ratios of 200. Clearly hydrocarbon consumption is not a reliable indicator of hydrocarbon reactivity with respect to photochemical oxidant production because of the importance of hydrocarbon ozonolysis.

Nitric oxide loss rates or NO to NO_2 conversion rates versus carbon/NO_x ratios are shown in Figure 7. Slow NO_x instrument response relative to the fast conversion of NO to NO_2 for the highly reactive terpenes at high carbon/NO_x ratios prevent accurate determinations of NO loss rates. However, the low capacity for driving the NO photooxidation of p-cymene compared to the other compounds is clearly shown in this figure.

On the basis of hydrocarbon-OH reaction a large number of hydrocarbons have been classified relative to their rate of OH reaction (17, 18). Compounds such as 3-carene, d-limonene, and myrcene are placed in the most reactive group. Propylene, isoprene, alpha-pinene, beta-pinene and p-cymene are placed in a group of lower reactivity. Although a scale based on OH reaction rate may be an indicator of a hydrocarbon atmospheric lifetime and its ability to oxidize NO it may not reflect the photochemical oxidant potential of a compound or other important parameters such as aerosol formation, eye irritation or plant damage. As reported earlier the most reactive compounds at higher carbon/NO_x ratios do not allow ozone to build up because of their extremely fast reaction with ozone.

An interesting phenomena was observed in some of the d-limonene irradiations: a double ozone maxima. Figures 36-B thru 38-B show the double peaks

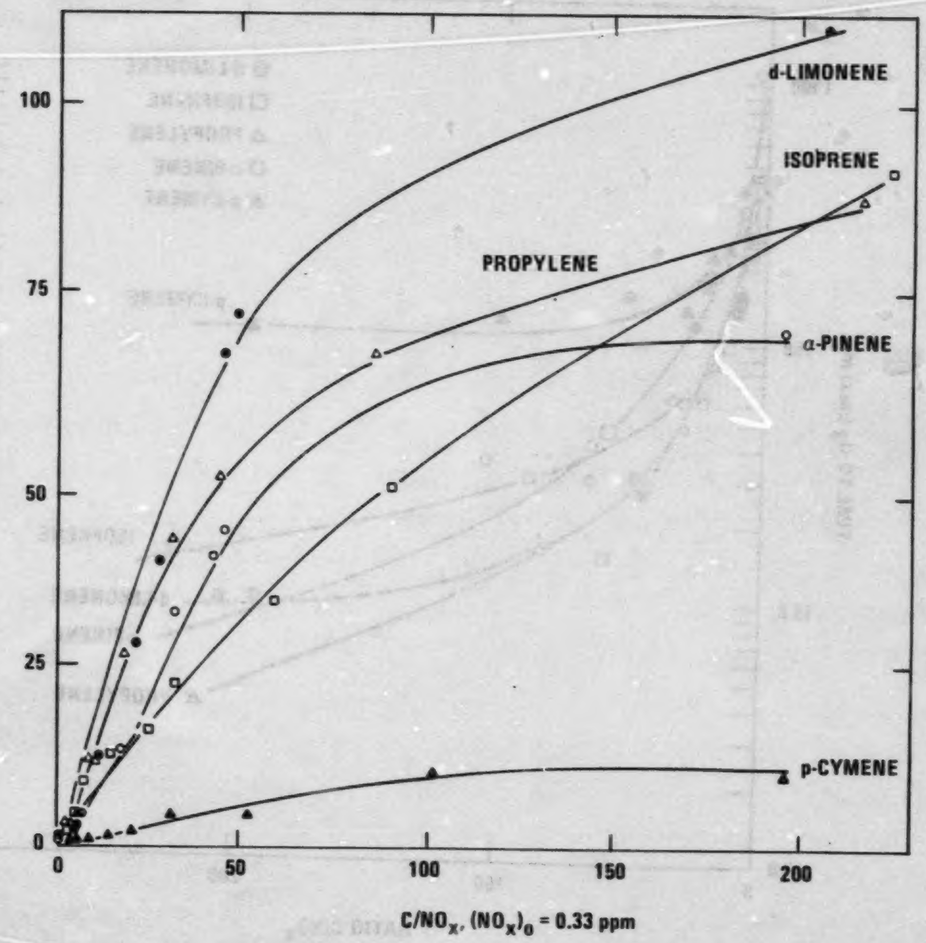


Figure 5. Effect of C/NO$_X$ ratio on hydrocarbon loss.

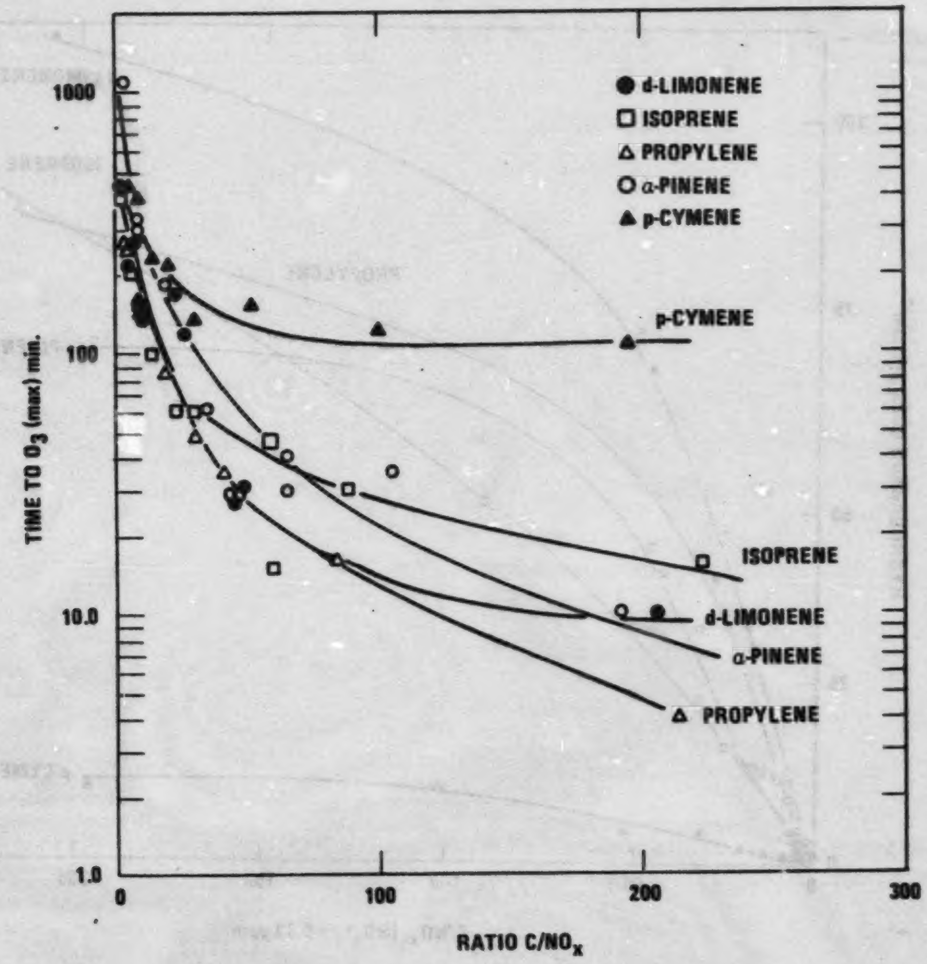


Figure 6. Effect of C/NO_x ratio on time to O_3 maximum.

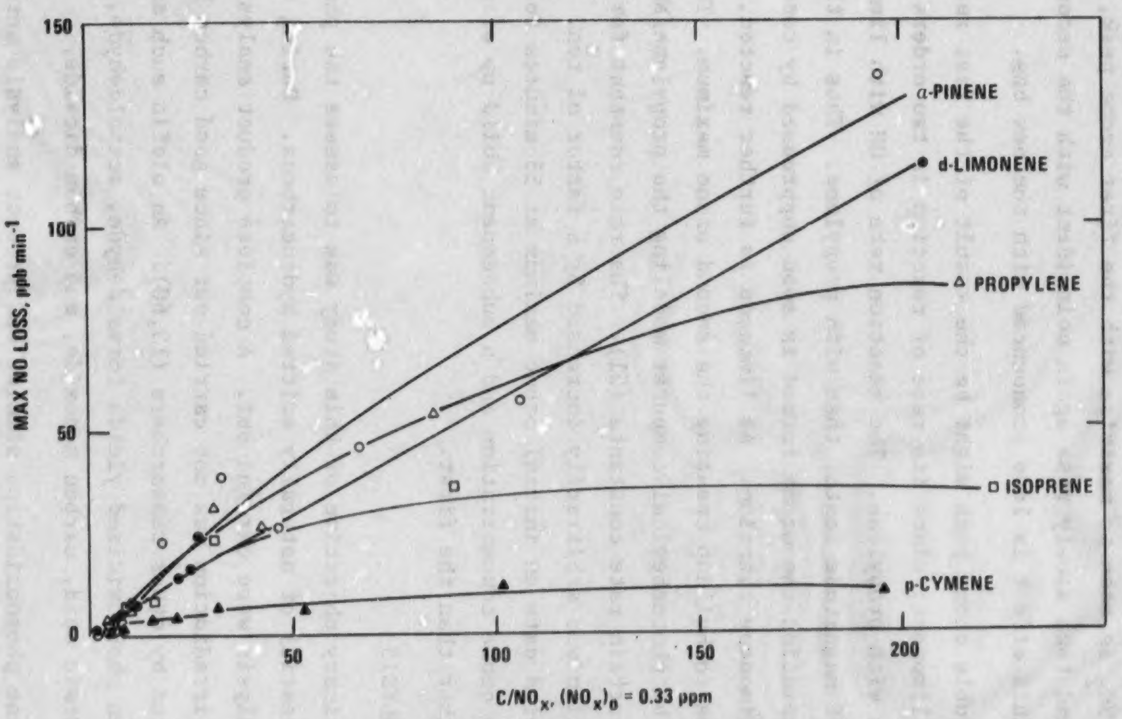


Figure 7. Effect of C/NO$_x$ ratio on NO loss (maximum).

seen only at C/NO_x ratios between 45 and 50. This anomaly is reproducible and was also observed in a new bag. New bags were used to verify that the original experiments were not a result of leaks or contamination from previous experiments. See figures 37-B and 38-B. Along with the ozone maxima the NO_2 is seen to maximize with the first ozone peak, quickly decrease, and then slowly rise again coincident with the second ozone maximum. This effect is less pronounced with the new bag.

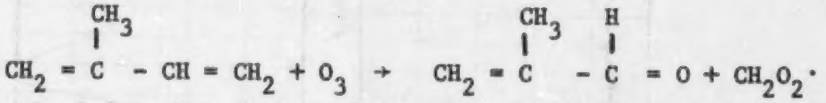
The double ozone peak might be the result of the fast reaction of ozone with limonene; since its rate of reaction is two orders of magnitude faster than with propylene. The reaction rate of OH with limonene is only one order of magnitude faster than with propylene. Thus in the early stages of the irradiation the ozone formed is soon suppressed by consumption of the ozone-limonene reaction. As limonene is further reacted, the ozone again begins to buildup creating the second ozone maximum. This effect was tested by photochemical computer modeling the propylene/NO_x system and adjusting certain rate constants (51). The rate constant for the propylene-ozone reaction was arbitrarily increased by a factor of ten. This produced in the modeled data an initial ozone maximum at 55 minutes followed by a decrease in ozone concentration and a subsequent build up of ozone to a maximum higher than the first.

PRODUCT ANALYSIS

The primary objective of this study was to assess the photochemical oxidant potential of naturally emitted hydrocarbons. During the irradiations product analysis were carried out. A complete product analysis of the propylene-NO_x irradiation was not carried out since good carbon balances have been reported by other researchers (13,60). An olefin such as propylene for example when photooxidized yields formaldehyde, acetaldehyde, peroxyacetylnitrate, formic acid, carbon monoxide, and carbon dioxide.

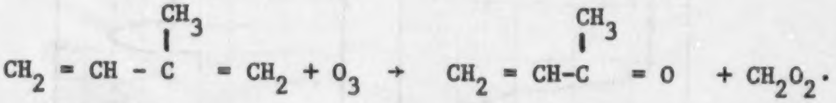
Isoprene photooxidation studies and product analysis were carried out by Schuck and Doyle in the 1950's (13). Their analysis of products formed in the irradiation of an isoprene-NO_x mixture at 100 minutes accounted for 87% of the reacted isoprene as formaldehyde, acetaldehyde, acrolein, peroxyacetylnitrate and carbon monoxide. Products were identified by their characteristic infrared absorption bands using long path infrared spectroscopy.

In our study of the irradiated isoprene-NO_x system using long path infrared spectroscopy the following reaction products and associated absorption frequencies were observed: acetaldehyde 2705 cm^{-1}, carbon dioxide 2355 cm^{-1}, carbon monoxide 2160 cm^{-1}, formaldehyde 2780 cm^{-1}, formic acid 1105 cm^{-1}, methacrolein 932 cm^{-1}, methylvinyl ketone 932 cm^{-1}, nitric acid 986 cm^{-1}, ozone 1055 cm^{-1} and peroxyacetyl nitrate 1162 cm^{-1}. Figures 8 shows the spectrum of the photooxidized mixture of 15 ppm isoprene and 7.5 ppm NO_2 after 45 minutes of irradiation. Shown in Figure 9 are the infrared spectra of the pure compound methacrolein and methyl vinyl ketone and the reaction mixture of photooxidized isoprene. No acrolein was detected in the photooxidation of isoprene either by infrared spectroscopy or gas chromatography. Mass spectral identification of methacrolein was also obtained for a photooxidized sample of isoprene in addition to methyl vinyl ketone. The product Schuck and Doyle identified as acrolein was most likely methacrolein. Methacrolein is formed by reaction of ozone across the 3-4 carbon-carbon double bond of isoprene.



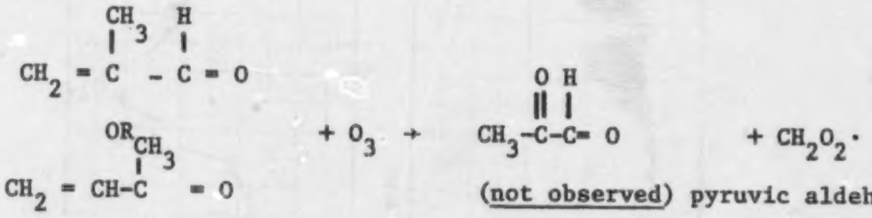
$$CH_2=\overset{CH_3}{\overset{|}{C}}-CH=CH_2+O_3\rightarrow CH_2=\overset{CH_3}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}=O+CH_2O_2\cdot$$

Reaction across the 1-2 carbon double of isoprene results in the formation of methyl vinyl ketone.



$$CH_2=CH-\overset{CH_3}{\overset{|}{C}}=CH_2+O_3\rightarrow CH_2=CH-\overset{CH_3}{\overset{|}{C}}=O+CH_2O_2\cdot$$

These two oxygenated olefinic products are still very reactive. Their concentrations in an irradiation maximize before that of ozone as shown in Figures 1-B to 9-B. Interestingly pyruvic aldehyde an expected common product of ozone reaction with methacrolein and methyl vinyl ketone, was not observed using long path infrared or gas chromatography.



$$\left.\begin{array}{l} CH_2=\overset{CH_3}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}=O \\ \text{OR} \\ CH_2=CH-\overset{CH_3}{\overset{|}{C}}=O \end{array}\right. + O_3 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{C}}=O + CH_2O_2\cdot$$

(not observed) pyruvic aldehyde

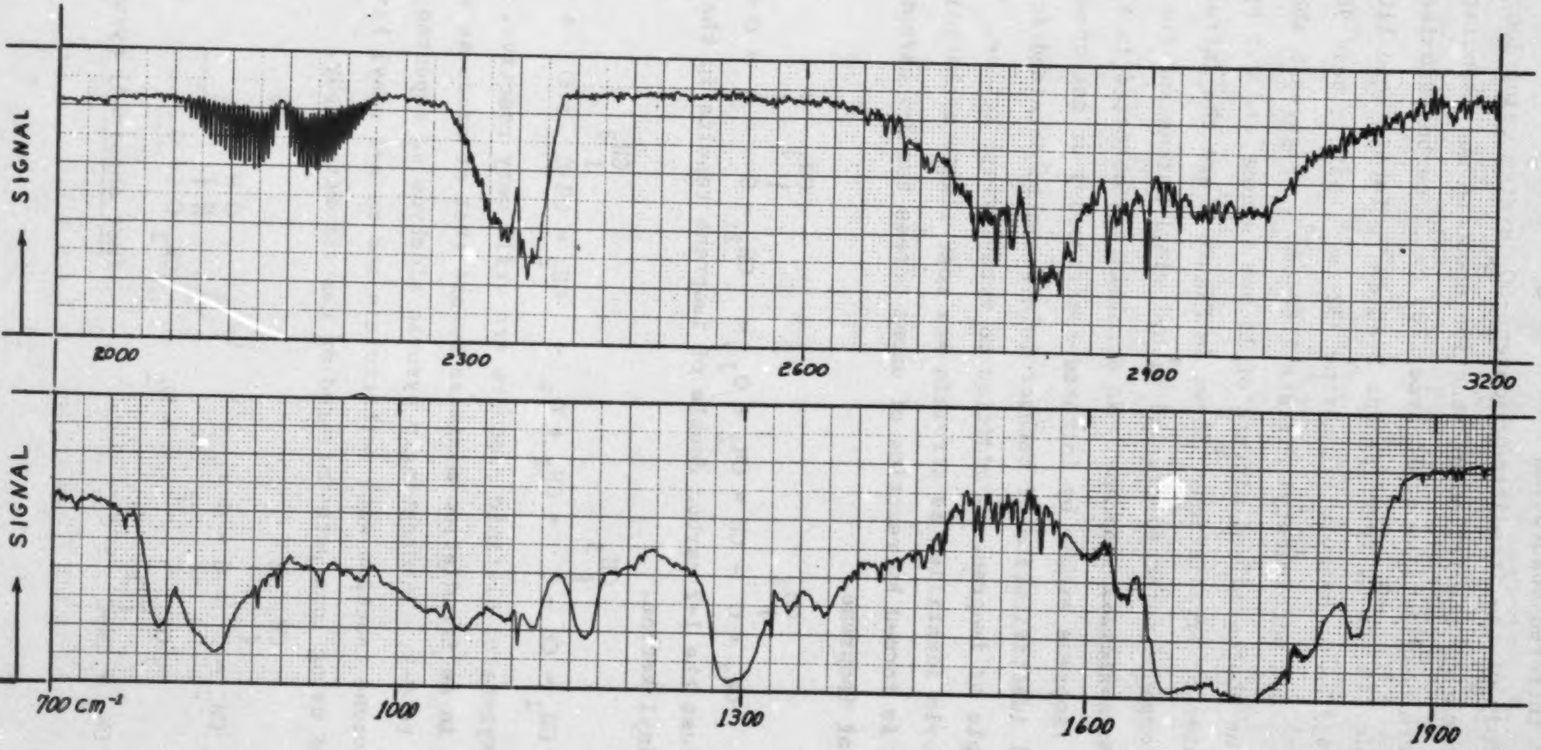


Figure 8. Spectrum of products of isoprene (15 ppm) and NO_2 (7.5 ppm). 45 min. irradiation · $k_{dNO_2} \simeq 0.7$ min.$^{-1}$, 216 meter path length.

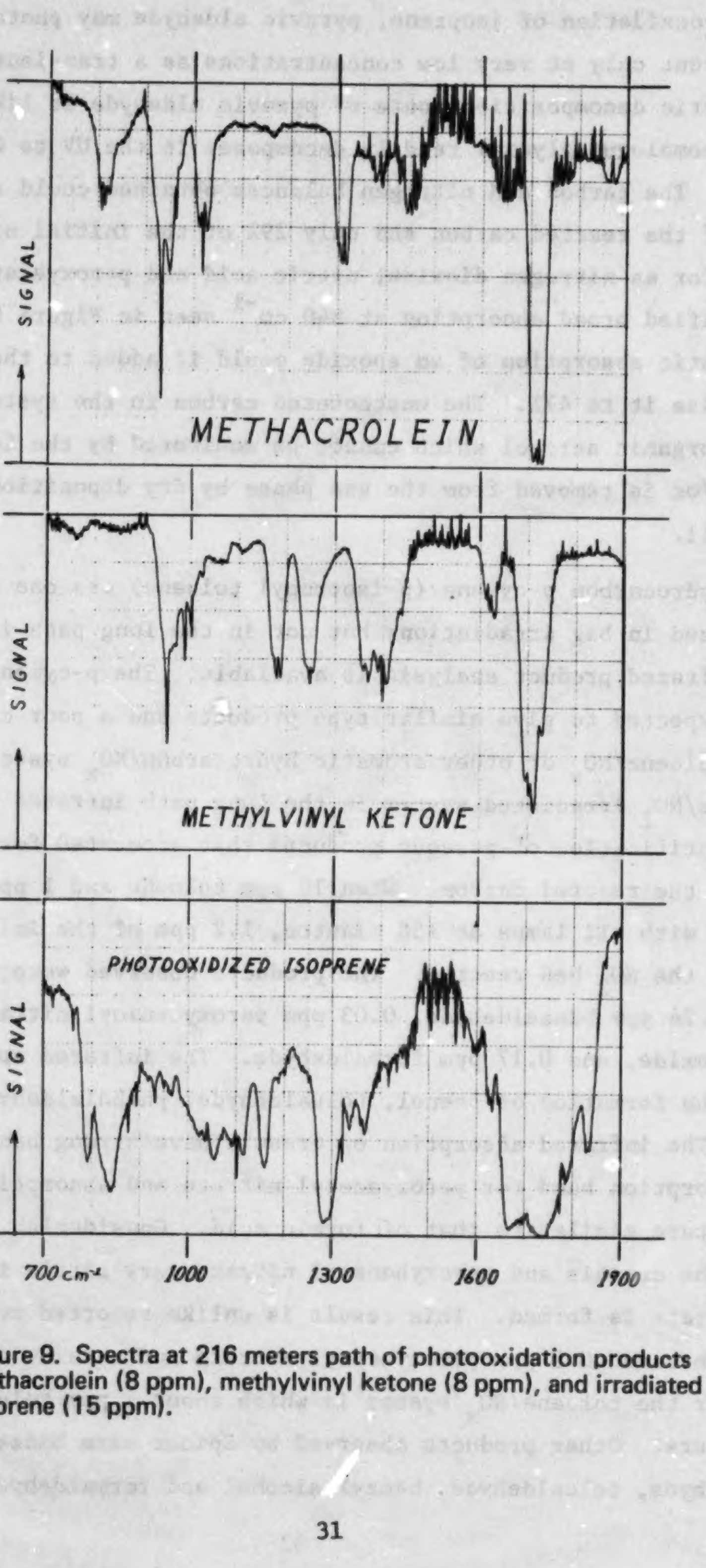


Figure 9. Spectra at 216 meters path of photooxidation products methacrolein (8 ppm), methylvinyl ketone (8 ppm), and irradiated isoprene (15 ppm).

In the photooxidation of isoprene, pyruvic aldehyde may photolyze quickly and be present only at very low concentrations as a transient species. The photolytic decomposition route of pyruvic aldehyde is likely since its lower homologue glyoxal readily decomposes in the UV to CO and CH_2O (61). The carbon and nitrogen balances obtained could account for only 44% of the reacted carbon and only 29% of the initial nitrogen was accounted for as nitrogen dioxide, nitric acid and peroxyacetyl nitrate. An unidentified broad absorption at 840 cm^{-1} seen in Figure 8 with characteristic absorption of an epoxide could if added to the carbon balance raise it to 47%. The unaccounted carbon in the system has either formed an organic aerosol which cannot be monitored by the long path infrared system and/or is removed from the gas phase by dry deposition onto the reactor wall.

The hydrocarbon p-cymene (p-isopropyl toluene) was one of the compounds photooxidized in bag irradiations but not in the long path infrared chamber. Thus no infrared product analysis is available. The p-cymene/NO_2 system would be expected to give similar type products and a poor carbon balance like the toluene/NO_x or other aromatic hydrocarbon/NO_x system. Studies of the toluene/NO_2 irradiated system in the long path infrared chamber resulted in the identification of gaseous products that accounted for less than 50 percent of the reacted carbon. When 10 ppm toluene and 1 ppm NO_2 were irradiated with all lamps at 158 minutes, 1.2 ppm of the initial toluene and all of the NO_2 had reacted. The products observed were 0.25 ppm cresols, 0.24 ppm benzaldehyde, 0.03 ppm peroxybenzoyl nitrate, 0.23 ppm carbon monoxide, and 0.17 ppm formaldehyde. The infrared spectra did not indicate the formation of phenol, tolualdehyde, phthalaldehydes or benzyl alcohol. The infrared absorption of cresols have strong bands at 1162 cm^{-1} a unique absorption band for peroxyacetyl nitrate and absorption at 1105 cm^{-1} with structure similar to that of formic acid. Considering all absorption bands of the cresols and peroxybenzoyl nitrate very little if any peroxyacetyl nitrate is formed. This result is unlike reported results of Spicer (62) who observed 0.3 ppm peroxyacetyl nitrate and obtains a 96% carbon balance for the toluene/NO_x system in which about 1 ppm toluene reacted in four hours. Other products observed by Spicer were benzaldehyde, cresols, phthalaldehyde, tolualdehyde, benzyl alcohol and formaldehyde.

Six monoterpenes: α-pinene, β-pinene, Δ^3-carene, myrcene, d-limonene, terpinolene, and isoprene were irradiated in the long path infrared chamber. Each hydrocarbon at an initial concentration of 8 ppm compound and nitrogen dioxide concentration of 1.2 - 1.5 ppm were irradiated at a $k_{d(NO_2)} = 0.51$ min^{-1}. The series of spectra shown in Figure 10 to 16 are for these compounds. The lower spectra in these figures noted as A are of the system after 60 minutes of irradiation and contains all the spectra information pertinent to gas phase species after this period of irradiation. The products observed in these systems at 60 minutes irradiation time are listed in Table 4. The spectra shown in Figures 10 to 16 also contain spectra of each system at 30 minutes (spectrum B), 10 minutes (spectrum C), and sample at time equal zero or before irradiation (spectrum D). In all these figures note the decrease in nitrogen dioxide concentration as observed by the decrease in absorbance of its infrared band at 1600 cm^{-1} as irradiation time increases from upper spectrum D, (t=0 minutes) to lower spectrum A, (t=60). This spectral evidence reinforces the earlier statements made about nitrogen dioxide chemiluminescence measurements remaining erroneously higher after the NO_2 maximum. Except for beta-pinene where only 0.01 ppm peroxyacetylnitrate was produced after 60 minutes of irradiation the infrared spectrum show vividly its formation. In contrast maximum PAN had formed after just 10 minutes of irradiation of the myrcene-NO_x mixture shown in Figure 13 (absorbance at 1162 cm^{-1}). The carbon balances in general were poor for all systems. The products that were obtained do offer some insight into the fragmentations or lack of fragmentation that takes place during photooxidation. Only about 9% of the carbon can be accounted for as gaseous products in the alpha-pinene system (Table 3). The reduction in the over all infrared absorption in the C-H region of the spectra (2850-3050 cm^{-1}) with time with minimal increase in absorption elsewhere implies that products are being removed from the gas phase. Processes including aerosol formation with subsequent wall deposition of aerosol material are probably occurring in the chamber.

In the ozonolysis of alpha-pinene Spencer (31) observed a white mist which when analyzed consisted of five oxygen atoms combined with each molecule of alpha-pinene which resulted in a $C_{10}H_{14}O_5$ compound. By classical qualitative techniques it was postulated that the compound had one of two structures.

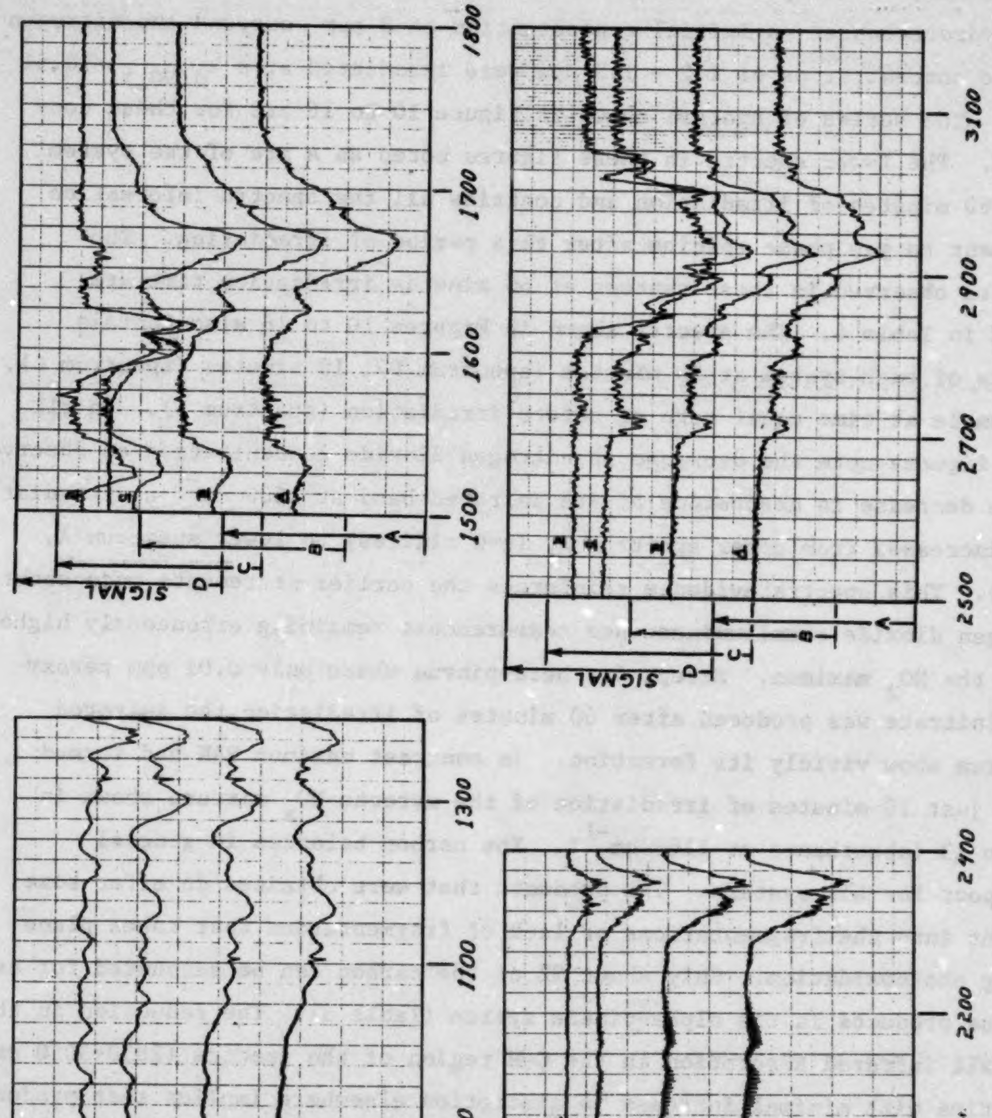


Figure 10. Spectra of alpha - pinene irradiation. Irradiation times: A = 60 min., B = 30 min., C = 10 min., D = 0 min. 357 meters path length, initial concentration alpha - pinene = 8 ppm, NO_2 = 1.2 ppm.

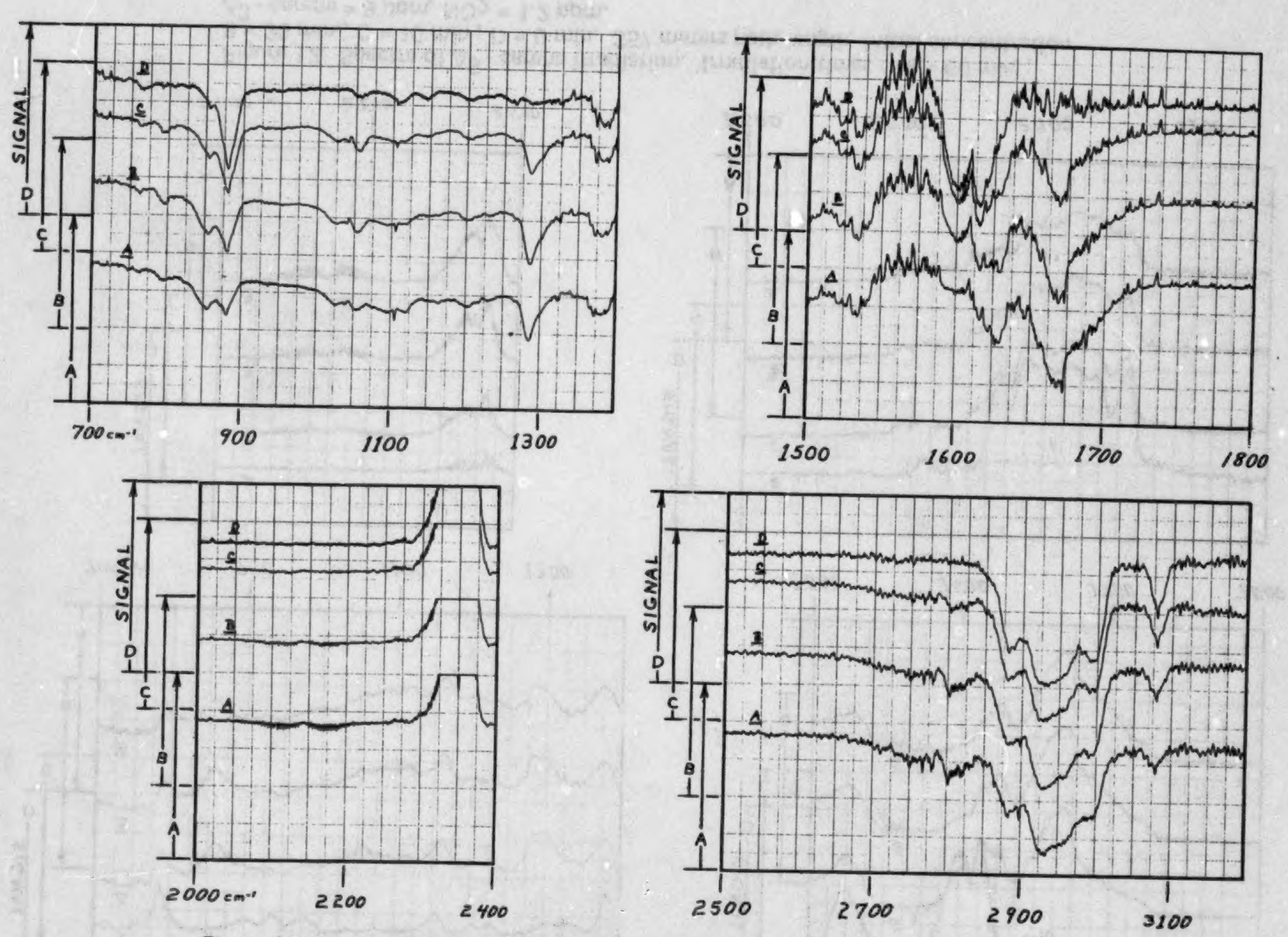


Figure 11. Spectra of beta - pinene irradiation. Irradiation times : A = 60 min., B = 30 min., C = 10 min., D = 0 min. 357 meters path length, initial concentration beta - pinene = 8 ppm, NO_2 = 1.5 ppm.

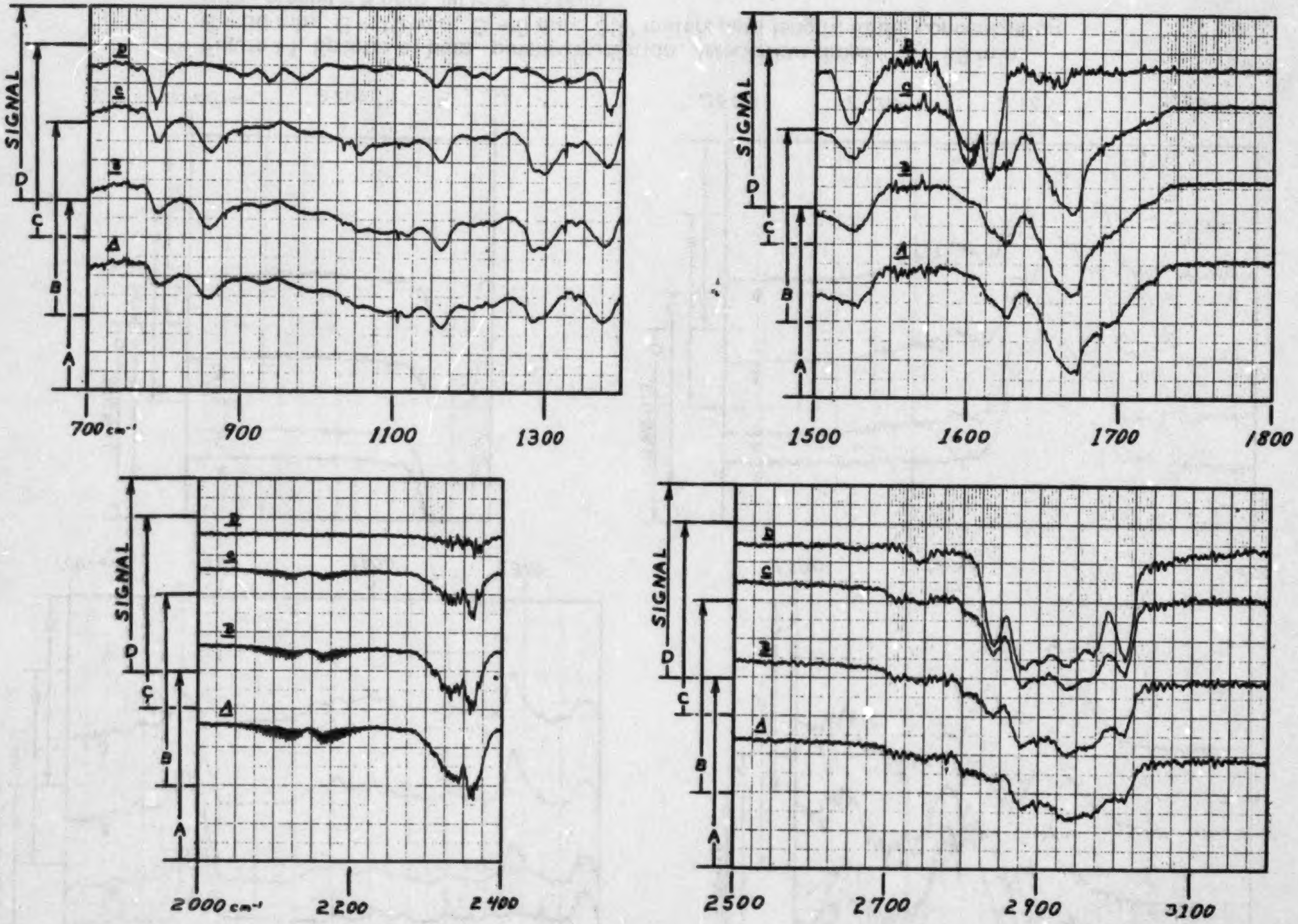


Figure 12. Spectra of Δ^3 - carene irradiation. Irradiation times : A = 60 min., B = 30 min., C = 10 min., D = 0 min. 357 meters path length, initial concentration Δ^3 - carene = 8 ppm, NO_2 = 1.2 ppm.

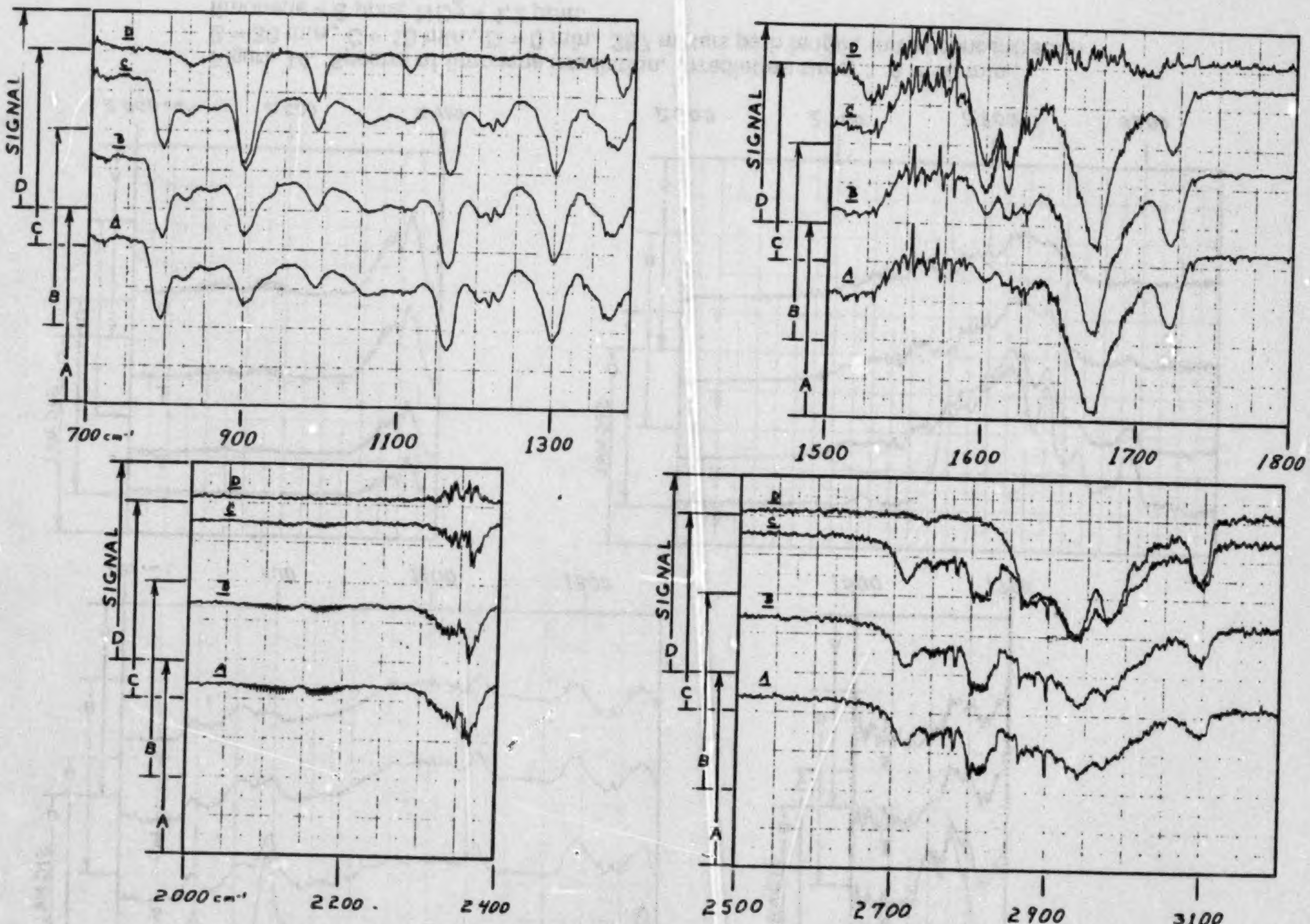


Figure 13. Spectra of myrcene irradiation. Irradiation times : A = 60 min., B = 30 min., C = 10 min., D = 0 min. 357 meters path length, initial concentration myrcene = 8 ppm, NO_2 = 1.3 ppm.

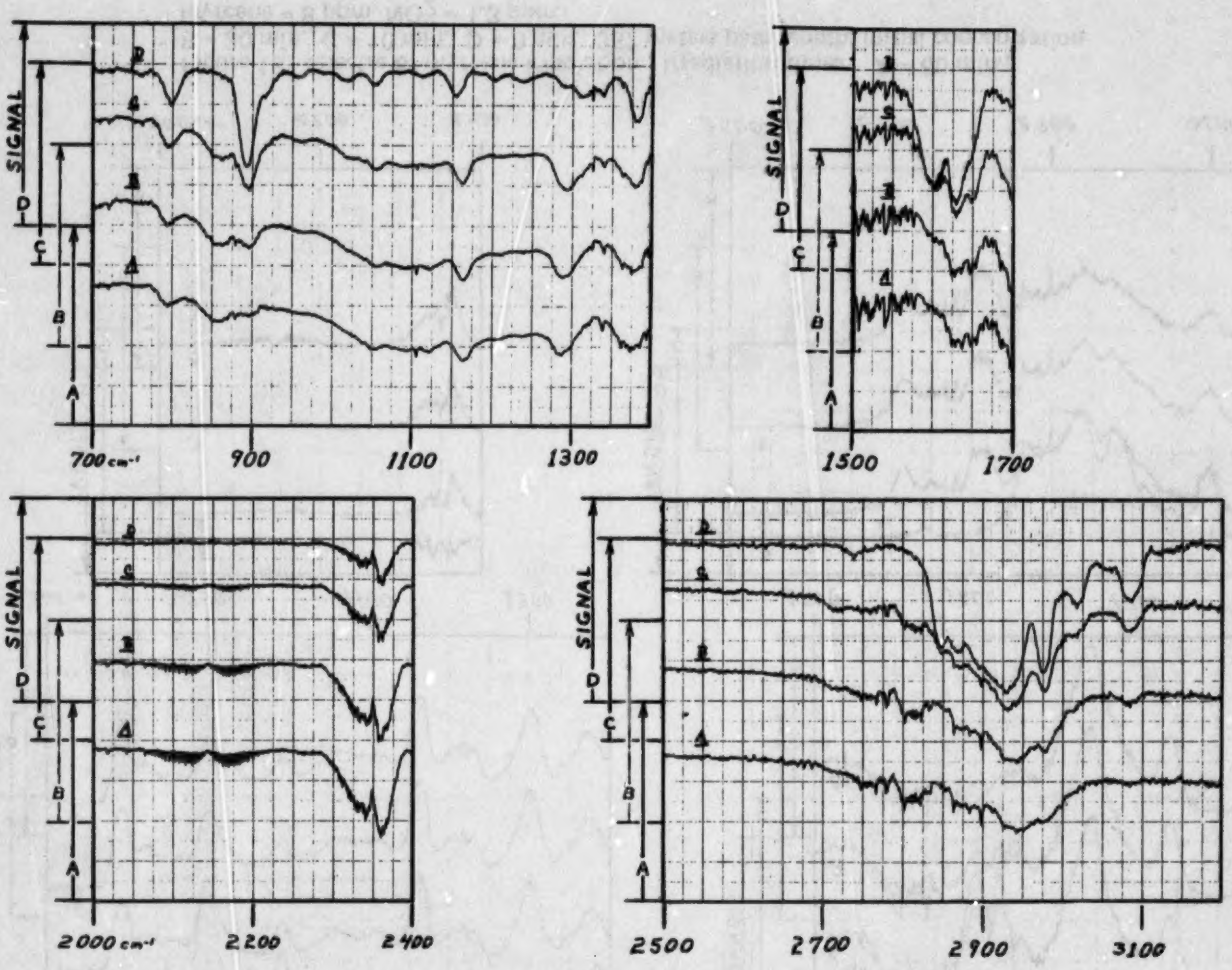


Figure 14. Spectra of limonene irradiation. Irradiation times : A = 60 min., B = 30 min., C = 10 min., D = 0 min. 357 meters path length, initial concentration limonene = 8 ppm, NO_2 = 1.2 ppm.

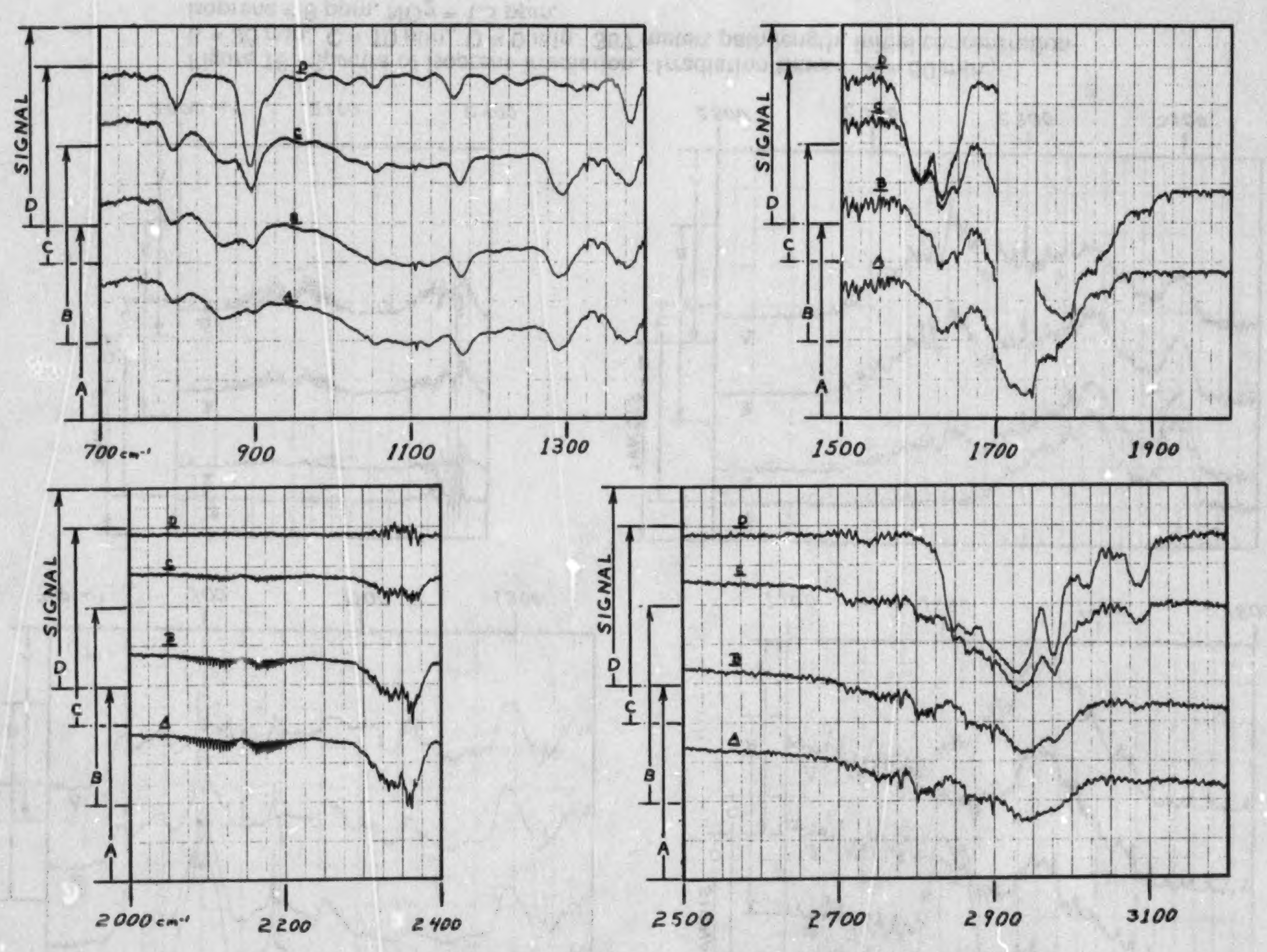


Figure 15. Spectra of terpinolene irradiation. Irradiation times : A = 60 min., B = 30 min., C = 10 min., D = 0 min. 357 meters path length, initial concentration terpinolene = 8 ppm, NO_2 = 1.3 ppm.

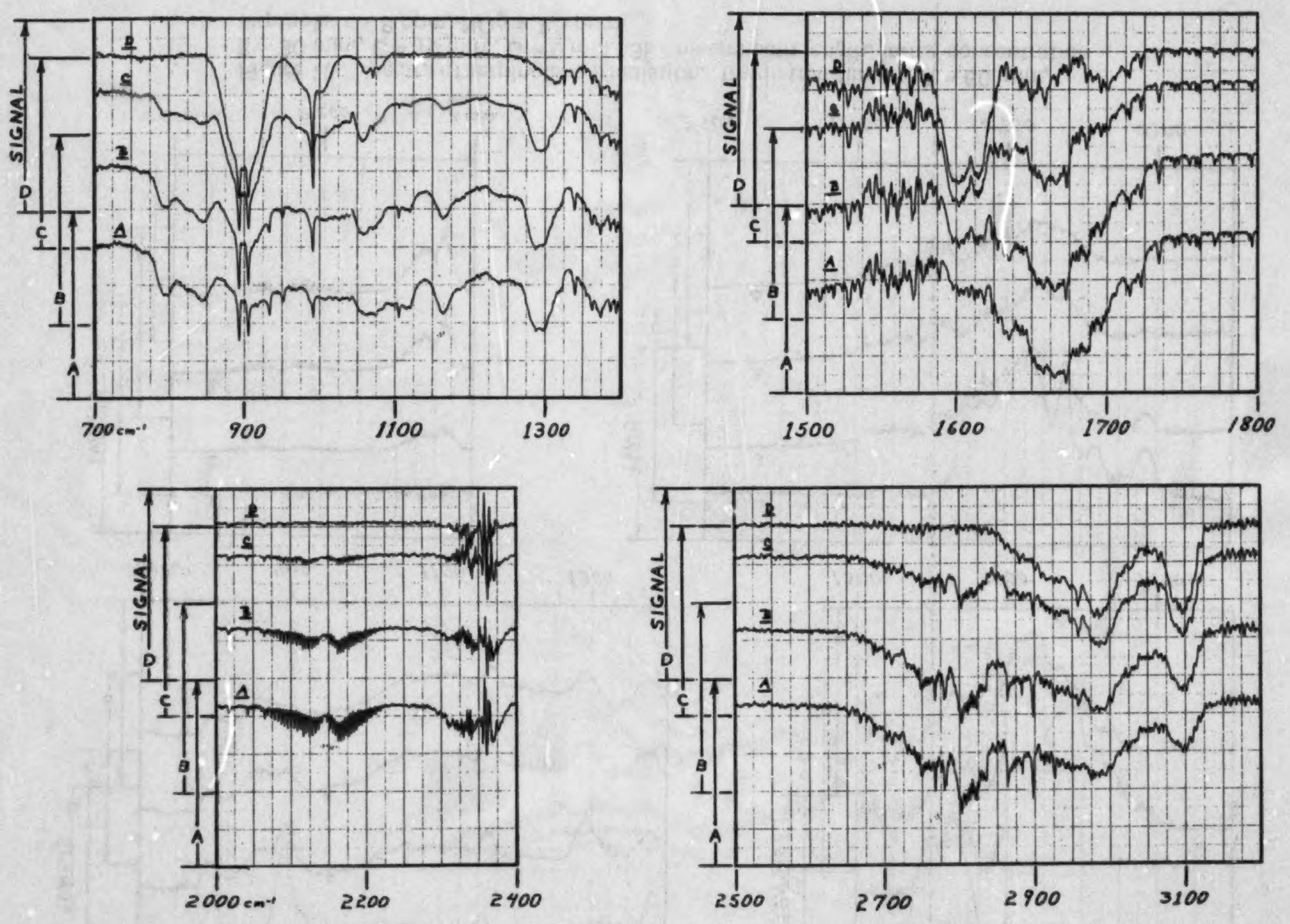
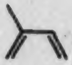
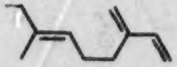
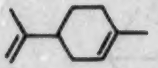
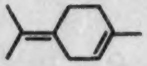
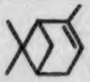
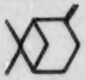
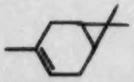


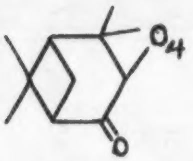
Figure 16. Spectra of isoprene irradiation. Irradiation times : A = 60 min., B = 30 min., C = 10 min., D = 0 min. 357 meters path length, initial concentration isoprene = 8 ppm, NO_2 = 1.3 ppm.

TABLE 4. REACTIVITY AND PRODUCTS BY LONG PATH INFRARED AT 60 MINUTES

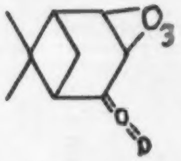
Compound	C/NO$_x$ ratio	%HC reacted	H_2CO	HCOOH	CO	CO_2	CH_3CHO	PAN	$(CH_3)_2CO$	Total ppmC products	% Carbon accounted for
Isoprene	31	68	2.39	0.44	0.77	0.2	2.0	0.32	0	8.44	31
	10*	100	6.8	3.4	4	2.0	1.95	1.2	0	32.8	44
Myrcene 	62	73	0.84	0.16	0.26	0.24	2.35	0.70	0.76	9.88	17
d-Limonene 	67	91	0.9	0.35	0.46	0.49	0.23	0.24	0	3.14	4
Terpinolene 	62	95	1.2	0.31	0.49	0.69	0.35	0.28	0	3.95	5
α-Pinene 	67	72	0.33	0.32	0.39	0.6	1.57	0.20	0	5.18	9
β-Pinene 	53	58	0.94	0.39	0.23	0.4	0.05	0.018	0	2.58	6
Δ^3-Carene 	67	60	0.46	0.39	0.50	0.9	0.33	0.26	0	3.43	7

Initial hydrocarbon conc. = 8 ppm
Products as ppm compound (v/v)
$k_d(NO_2) = 0.51\ min^{-1}$

*Initial concentrations: 15 ppm isoprene, 7.5 ppm NO_2; irradiated for 45 minutes; additional products detected; 1.0 ppm methacrolein, 1 ppm methyl vinyl ketone, 0.5 ppm HNO_3, 1.1 ppm O_3, 0.5 ppm NO_2 (remaining)



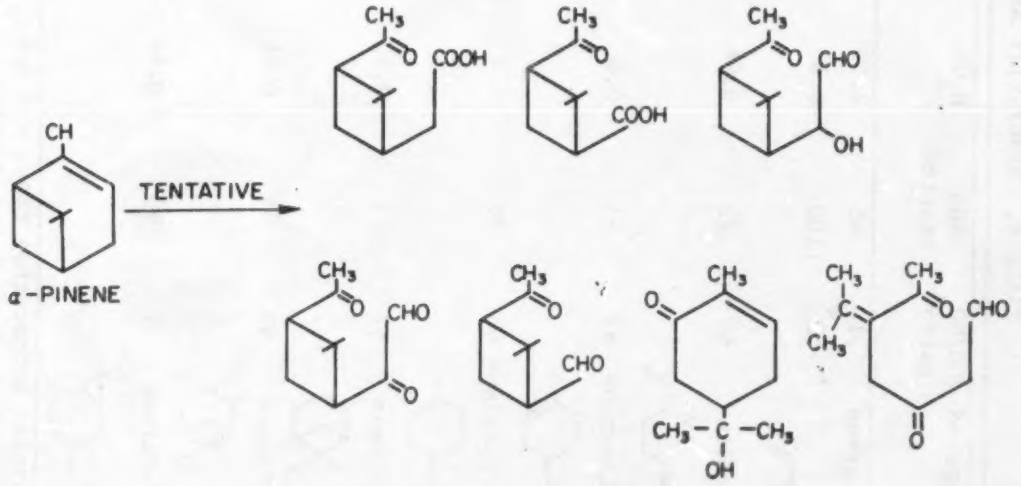
Verbenone
Oxozonide



Verbenone peroxide
Ozonide

Other researchers have also collected aerosols formed from the alpha-pinene/ NO_x irradiated system and obtained infrared absorption spectra (21, 23, 24, 28). The prominent absorption obtained of the aerosols is characterized by the carbonyl (-C=O) stretching frequencies. Wilson, *et al*. (30) obtained similar infrared absorption spectrum for the dichloromethane extracted fraction of smog chamber generated alpha-pinene aerosols and aerosols collected in the pine forested Blue Ridge Mountains of North Carolina. The same researchers also performed extensive extraction, derivatization, and gas chromatographic-mass spectral analysis in attempts to identify components comprising the alpha-pinene/NO_x aerosol. Hampered by a lack of reference standards these investigators were able to confirm only one compound in the acid extraction: pinonic acid. A number of oxygenated species were postulated based on mass spectral analysis of the derivatives of acid, base, and neutral fractions shown below.

Postulated Oxygenated Species of Alpha-Pinene (26)



Somewhat surprising is the fact that nitrogen containing aerosol compounds were not detected. Nitrogen containing aerosols would be expected in the alpha-pinene/NO_x irradiated system because of the poor nitrogen as well as carbon balance.

Pinonic acid was identified in collected aerosol sample of the Pisgah National Forest of western North Carolina but was absent in urban samples (30). Due to the semiquantitative nature of the study of the alpha-pinene to pinonic acid aerosol process it is not possible to estimate what portion of the forest aerosol samples are due to alpha-pinene oxidation. However, as noted prevously infrared spectra of the dichloromethane extractable fraction of forest and chamber samples did compare favorably.

Two monocyclic diolefin terpenes d-limonene and terpinolene gave similar gaseous products as shown in Table 4. These observed gaseous products represent less than 10% of the reacted carbon. Unidentified weak absorption bands were observed at 855, 1630, and 1650 cm^{-1} in the d-limonene irradiation and 853, 1290, 1375, and 1630 cm^{-1} in the terpinolene irradiation. In neither case assuming the most favorable absorption coefficients would the unidentified absorption account for more than a few percent of the reacted carbon. The formation of aerosol is the probable cause of the carbon balance deficiency (25).

Two bicyclic mono-olefins Δ^3-carene and beta-pinene like the other compounds also have poor carbon balances. Gaseous product identification is shown in Table 4. Less than 10% of the reacted carbon can be accounted for as gaseous products. Again aerosol formation probably accounts for much of the unaccounted for carbon. The infrared analysis of aerosol generated from beta-pinene and alpha-pinene were carried out by Stephens and Price (28). The only prominent characteristic absorption was the carbonyl region around 1700 cm^{-1} for both terpene aerosols. The only previously reported study of the photochemistry of Δ^3-carene was the work of Grimsrud et al. (16) but products were not determined.

Myrcene was different than any of the other C_{10} monoterpenes studied since it is acyclic and possessed the greatest number of olefinic bonds: three. The amount of myrcene reacted in 60 minutes and analysis of gaseous products are given in Table 4. The high yield of acetaldehyde, peroxyacetyl nitrate and acetone along with other observed products account for 17% of the reacted carbon. While this is still a relatively poor carbon balance, it is still significantly better than the cyclic terpene systems previously described. The open chain structure of myrcene compared to the cyclic terpenes apparently fragments more easily into volatile low molecular weight oxygenates. The monocyclic diolefins and the bicyclic mono-olefins when reacted with hydroxyl radicals or with ozone across the double bond form monofunctional oxygenated cyclic compounds or difunctional ring opened oxygenated compounds. These compounds are expected to be low in volatility and condense out as aerosols.

In addition to the long path IR studies a sensitive high resolution gas chromatographic study was performed to help identify terpene oxonolysis products. Using the cryogenic trapping procedures and the 3 column FID system described by Lonneman (8) analyses were made on 5 ppm (v/v) terpene air samples which were reacted with excess ozone. The chromatographic procedure will in general separate C_1-C_{10} hydrocarbons and some of their oxygenates. Unfortunately, very little of the products could be detected. Small amounts (less than 1%) of acetaldehyde could be seen. It is probable that the products condensed to form aerosols or being extremely polar were unable to pass through the chromatographic columns for detection.

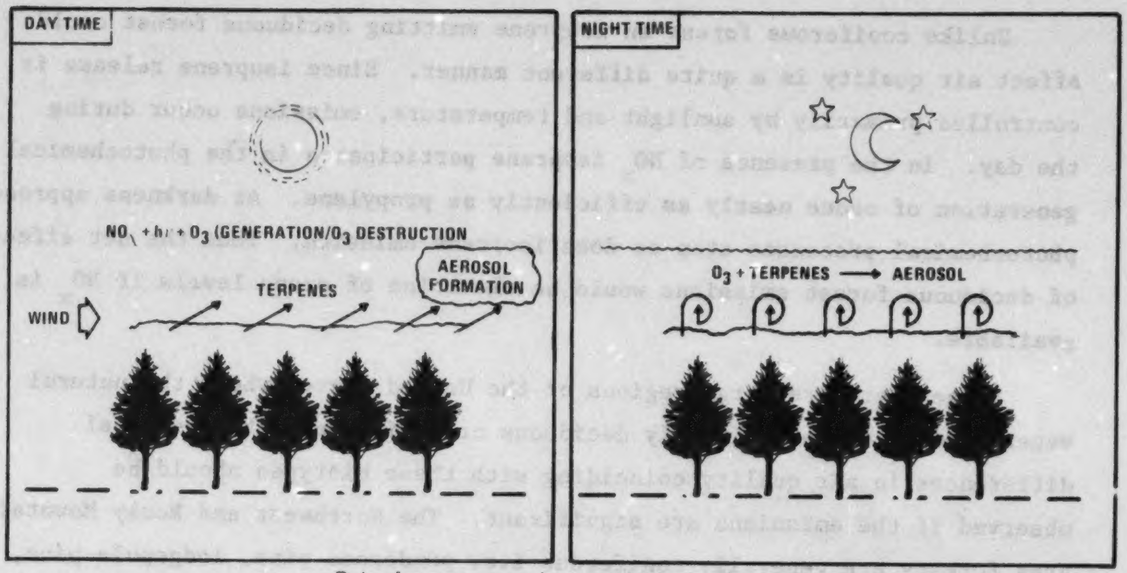
The phenomena of aerosols formation should be considered when attempting to apply laboratory smog chamber results to real atmospheric conditions. In these reported smog chamber experiments the initial hydrocarbon concentrations were 10 to 1000 times higher than any reported natural hydrocarbon concentration in the ambient atmosphere. Since many of the olefins react extremely fast with ozone an accumulation of ozone is suppressed at high carbon/NO_x ratios. At these higher hydrocarbon concentrations the concentrations of oxygenates formed are also higher which result in aerosol formation. Recent studies have shown there is a threshold hydrocarbon concentration below which aerosol formation does not occur (23,63,64). Since aerosol formation represents a chain termininating step in the photochemical mechanism its effect is the removal of partially oxidized hydrocarbons from the system before the maximum ozone generating potential is realized. Caution should be excercised in extrapolating the ozone producing ability of a compound at high concentrations to ambient concentrations where aerosols may not be formed. At low ambient natural hydrocarbon concentration the oxygenated hydrocarbons could remain in the gas phase and continue to react in the photochemical system. However, results of experiments at 100 ppbC (a value which approaches an upper limit of ambient terpene concentrations) and 10 ppb NO_x show propylene to be significantly more efficient than α-pinene in producing ozone (see Table 3).

EFFECT OF VEGETATION ON AIR QUALITY

A number of the more common trees in the continental United States have been surveyed with respect to hydrocarbon emissions (3). It is generally found that the deciduous vegetation (hardwoods) are primarily isoprene emitters and conifers (softwoods) are basically monoterpene emitters. There are also several species of vegetation that emit both isoprene and monoterpenes. Some emission controlling environmental variables in plants have been found although the biochemical function of both isoprene and the monoterpenes is poorly understood. The monoterpenes at or close to the air plant interface accumulate in the resin ducts of the foliage (65). More difficult to quantitate are the significance of resin blisters which appear on the woody parts of the tree as a result of wounds, disease, or insect attack. Studies by Rasmussen (30), Dement _et.al_. (66), and Tingey _et al_. (67) show the rate of terpene volatilizing from foliage in environmental chambers depended upon temperature, vapor pressure of the emitted compound, and in some cases humidity. Tingey _et al_. (67) found foliage temperature rather than ambient air temperature to be a more accurate predictor of terpene emissions. In-situ measurements of α-pinene at a pine forest reported by Arnts _et al_. (38) did not show a strong correlation of hydrocarbon flux with ambient air temperature. The α-pinene flux in this study was found to correlate directly with temperature and inversely with windspeed. This suggests a dependence on foliage surface temperature rather than air temperature.

In contrast with the monoterpenes, isoprene emission are strongly dependent on sunlight. Rasmussen and co-workers (34,35,68,69) have shown that isoprene emission mostly by deciduous plants occurs predominately in sunlight and is therefore probably directly linked to photosynthesis. Unlike the monoterpenes which can continue to volatilize from the resin ducts in darkness, the much more volatile isoprene does not appear to be stored by the plant for release at night. Recent studies by Tingey et. al (70) confirm the sunlight dependence of isoprene emissions. Live oaks were found to saturate with moderate light intensities, the study also revealed that temperature became a controlling variable at a given light intensity. The study concluded that after reaching moderate light intensities temperature becomes the rate controlling variable.

Using emission characteristics of vegetation, chemical nature of the biogenic hydrocarbons, and a consideration of boundary layer micrometeorology the air quality of forest airsheds can be visualized. Figure 17 illustrates the influence of a coniferous forest on the day and nighttime air quality. During the daytime terpenes are volatilized as the temperature increases. Terpenes emitted into the atmosphere react with species such as O_3 and OH to principally form aerosols and if sufficient NO_x is present ozone and additional aerosol products are formed. At night terpenes are emitted at a lower rate due to cooling biomass; nighttime inversions tend to trap the terpenes within the boundary layer which may be as low as the tree canopy crown. In the absence of sunlight to initiate photochemical reaction the terpenes react with ozone forming principally aerosols. Evidence for nighttime ozone destruction has been observed at a pine forest site where ambient ozone and alpha-pinene concentrations have been monitored concurrently both above and below the forest canopy (40). Although dry deposition certainly accounts for some ozone destruction, elevated alpha-pinene concentrations below the canopy accompanied by suppressed ozone concentrations during predawn inversion conditions support this hypothesis. The highest concentrations of monoterpenes reported in the ambient atmosphere were measured in the forest canopy. The concentrations observed were on the order of 40-50 ppbC measured in the early morning hours (3-6 AM) but quickly declined to less than 10 ppbC as the inversion dispersed after


DAY TIME
NO$_x$ + hν + O$_3$ (GENERATION/O$_3$ DESTRUCTION
AEROSOL FORMATION
TERPENES
WIND
NIGHT TIME
O$_3$ + TERPENES → AEROSOL

Role of monoterpenes in atmospheric chemistry.

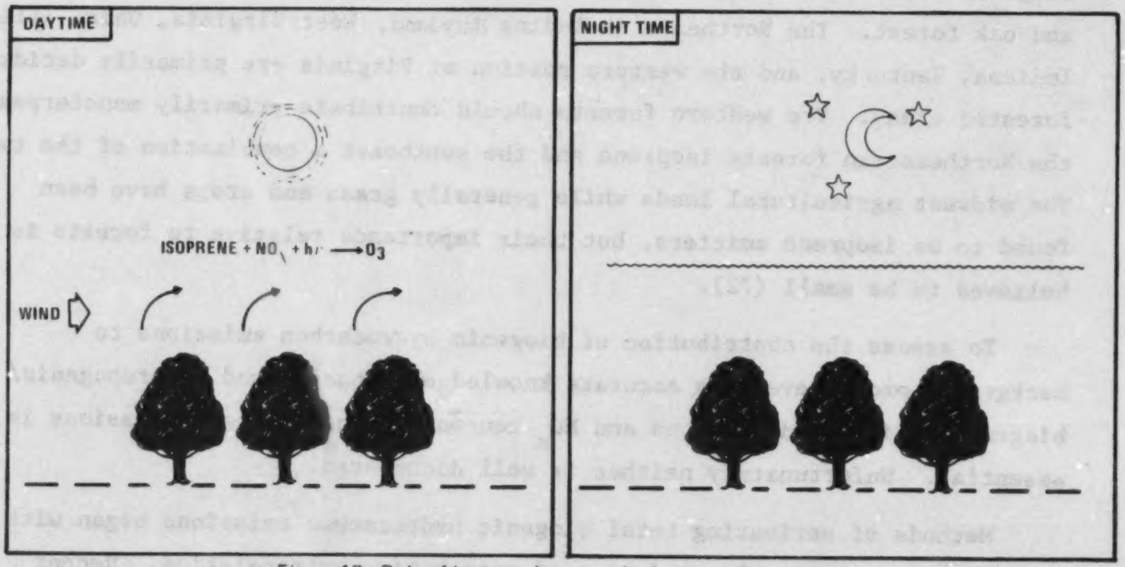

DAYTIME
ISOPRENE + NO$_x$ + hν → O$_3$
WIND
NIGHT TIME

Figure 17. Role of isoprene in atmospheric chemistry.

sunrise. The monoterpene emitting forests may actually destory more ozone than it creates since terpenes are very efficient at destroying ozone and create ozone inefficiently.

Unlike coniferous forest an isoprene emitting deciduous forest could affect air quality in a quite different manner. Since isoprene release is controlled primarily by sunlight and temperature, emissions occur during the day. In the presence of NO_x isoprene participates in the photochemical generation of ozone nearly as efficiently as propylene. As darkness approaches photochemical processes stop as does isoprene emission. Thus the net effect of deciduous forest emissions would be elevation of ozone levels if NO_x is available.

Since there are large regions of the United States where the natural vegetation is either primarily deciduous or coniferous, then regional differences in air quality coinciding with these biotypes should be observed if the emissions are significant. The Northwest and Rocky Mountains area forests are generally coniferous i.e. ponderosa pine, lodgepole pine, douglas fir, redwood (71). Large areas of the Southeast are predominately pine and oak forest. The Northeast including Maryland, West Virginia, Ohio, Illinois, Indiana, Kentucky, and the western portion of Virginia are primarily deciduous forested areas. The western forests should contribute primarily monoterpenes, the Northeastern forests isoprene and the southeast a combination of the two. The midwest agricultural lands while generally grass and crops have been found to be isoprene emitters, but their importance relative to forests is believed to be small (72).

To assess the contribution of biogenic hydrocarbon emissions to background ozone levels an accurate knowledge of background anthropogenic/biogenic ambient hydrocarbons and NO_x concentrations or their emissions is essential. Unfortunately neither is well documented.

Methods of estimating total biogenic hydrocarbon emissions began with one measurement and a large degree of presumptive extrapolation. Recent estimates use marginally refined measurements and equally commensurate imaginative extrapolations. An examination of the literature reviewed by Robinson and Robbins in 1968 (7) reveals some tenuous assumptions which can impart a great deal of uncertainty to the early emission estimates. The first estimate by Went (73) using unpublished data of Haagen-Smit involved extrapolating the emission rate of one sage brush plant to the vegetated surface of the earth. This estimate assumed (1) emission of this plant is representative of the same plant growing in the open environment, (2) a fixed rate of hydrocarbon release (5% volatiles released of the photosynthates formed) dependent on photosynthesis, (3) hydrocarbon release of other plants i.e. coniferous and to an arbitrarily lesser degree deciduous forests, agricultural lands and steppes are a similar proportion of volatiles. Even accepting the above assumptions extrapolations were performed using order of magnitude estimates of the land area covered by these vegetative types. Thus the first biogenic hydrocarbons estimate was an extremely crude but nevertheless interesting speculation on the subject.

Rasmussen and Went in 1965 (27) increased Went's previous estimate by employing two additional methods and including isoprene as a biogenic emission. They assumed a vertical column of 10 ppb organic volatiles averaged up to 2 km over the world vegetative surfaces. The isoprene: monoterpenes ratio making up the 10 ppb organic volatiles was not specified. Consequently this could represent a minimum concentration of 50 ppbC (assuming 100% isoprene) to a maximum 100 ppbC (assuming 100% monoterpene). The average 10 ppb organic volatiles is based on their ground level measurements only and is not supported by vertical profile measurements. Subsequent detailed hydrocarbon measurements by Lonneman (74), Rasmussen (75), and Holdren (76) analyzing both ground level and aircraft ambient air samples have never demonstrated maximum concentrations greater than 1/10th of the 10 ppb concentration; typically values are less than 1/100th this value levels. Arnts et al. (38) observed only a few ppbC of α-pinene a few meters above the canopy of a pine forest in North Carolina during the day. Holdren reported similar concentrations of monoterpenes in forested areas of the Northwest (76). Thus it appears that Rasmussen and Went's estimate is based on erroneous assumptions. They also arrived at an estimate of biogenic emissions based on emissions of vegetation placed in a plastic bag. The drawbacks of this technique and its derivatives will be discussed later.

Robinson and Robbins (7) in their review found that 66% of the atmospheric non-methane hydrocarbon loading should be of biogenic origin. The review has been widely cited in discussions of the efficacy of EPA hydrocarbon control regulations with a large amount of significance attached to the estimates. While ambituous in its scope the review did not attempt to critically review the limitations of its sources nor discuss the uncertainties inherent in their estimates.

Since the review of Robinson and Robbins other efforts have been made to quantitate biogenic hydrocarbon emissions. Rasmussen examined emissions of foliage enclosed in leaf assimilation chambers over a range of temperatures and illuminations (3). Data from these experiments were extrapolated to obtain estimates of global biogenic emissions. Recently Zimmerman (72) refined the enclosure techniques of Rasmussen to study more plant species. In these studies the dry weight of the plant parts are used to reference emission e.g. gm hydrocarbon emitted/gm dry weight foliage. A scaling factor (gm dry weight foliage/area of land surface area) derived from data gathered in the International Biological Program is used to develop regional emission factors and subsequent global emission estimates. While there is evidence to believe that the enclosure method tends to overestimate emissions (77), the larger problem probably lies in the accurate extrapolation of the emission factors to large land areas of mixed and discontinuous vegetation.

Research Triangle Institute proposed an upper limit for global biogenic emissions based on estimates of the total carbon fixed by green plants on the land surface of the world (1). They assumed that perhaps 10% of the total fixed carbon could represent an 'upper limit' of volatiles released by green plants. This estimate, some 20 times greater than Rasmussen and Went's estimate, represents assumptions based on order of magnitude estimates of total fixed carbon and an arbitrarily chosen 10% upper limit of total fixed carbon as volatiles.

Emission estimates to date for biogenic and probably to a lesser but significant degree for anthropogenic emissions are fraught with much uncertainty. All estimates of reported emissions to date state that the majority of hydrocarbons present in the well mixed continential air mass is of biogenic origin and as monoterpenes and isoprene. This has simply not been shown to be the case in any field study yet performed. Investigators find 'clean' air masses to be predominately photochemically olefin depleted dilute auto exhaust, i.e. contain C_2-C_5 alkanes and aromatics consisting primarily of benzene, toluene, and the xylenes. Monoterpenes in rural areas rarely exceed 10 ppbC and are frequently not detected at limits of detection less than 0.5 ppbC. Isoprene has been observed as high as 30 ppbC in a forested area near Boston (10). Washington State University (75) typically observed about 7 ppbC of isoprene in a lightly forested agricultural area of Missouri. In all cases biogenic hydrocarbons contributed no more than a maximum of 25% to the NMHC of a clean air mass which had a NMHC concentration of 80 ppbC or greater. Although arguments have been made that biogenic emissions react much faster than anthropogenic emissions, analysis of air samples collected at forests in the tree canopies where reactions would be considered negligible and emissions should be greatest have not shown a predominance of biogenic over anthropogenic hydrocarbons. Emission inventories therefore for both biogenic and anthropogenic hydrocarbons could be inaccurate. It is necessary to examine the detailed hydrocarbon analysis of a 'clean' air mass to determine anthropogenic and biogenic composition to relate their contribution to background ozone formation. The transport of hydrocarbons and other pollutants from urban centers has been well documented (10-12). The concentrations of urban tracer gases such as acetylene and CCl_3F can be used in addition to back trajectory analysis to establish the movement of the air mass. Accurate NO_x concentrations in the air mass must also be determined if the photochemical oxidant potential is to be estimated. If attention is not given to detailed hydrocarbon, NO_x analysis and air mass movement details background clean air status is incorrectly given to air masses which have been strongly influenced by anthropogenic sources. Recently, Whitehead and Severs (78) reported total non methane hydrocarbon analysis of ambient air samples collected in a forested area 38 miles north of Houston, Texas, which averaged 8.7

ppmC for 35 morning samples. The investigator concluded the TNMHC levels were produced by vegetation. The data as reported did not show conclusively the lack of influence by local anthropogenic sources. A detailed hydrocarbon analysis if performed by the investigator would have shown the anthropogenic and biogenic hydrocarbon make up of the air. Seila (79) has taken ambient air samples from the same forested area, conducted detailed hydrocarbon analyses and found TNMHC concentrations only 1/20th those measured by Whitehead and Severs. Of those air samples only 2% of TNMHC could be attributed to vegetative sources. This shows the necessity of conducting detailed hydrocarbon analysis of air samples to determine its anthropogenic and biogenic composition. A certain gas chromatographic expertise is needed in attempting detailed hydrocarbon air analysis.

In a paper by Whitby and Coffey (80) the authors propose that hydrocarbons measured in the ambient air of an Adirondack mountain pine forest are terpenes and their oxidation products. The analyses carried out by these investigators are suspect due to the use of a low resolution 6' packed column of OV-101. This column used to resolve terpenes will also elute C_9-C_{10} auto related aromatic compounds within the same retention times as the terpenes. These C_9-C_{10} aromatics compounds are found in a photochemically aged urban plume. Lonneman (personal communication) reports various laboratories have observed artifact or ghost peaks associated with the use of this particular column.

During a field study near Elkton, Missouri, (population 30) an area free from nearby urban centers researchers from Washington State University (75) conducted detailed hydrocarbon analysis on 80 ambient air samples. The results of this study indicated an average TNMHC of about 98 ppbC with a range of 41 to 150 ppbC. The influence of urban hydrocarbons was evident in samples at the higher TNMHC range. Monoterpenes were not observed which is consistent with the local deciduous vegetation. Isoprene was observed quite regularly at about 6 ppbC and had a range of less than 0.4 to 28 ppbC in all samples. Isoprene represented the single largest hydrocarbon species which on the average contributed only 6% to the measured TNMHC. In an extreme situation isoprene constituted 24% of the 108 ppbC TNMHC measured at 7:00 PM CDT with near zero surface winds.

Isoprene in ambient air samples has also been reported by Lonneman et al. in the 1975 Northeast oxidant study (81). The Chickatabut Hill sampling site 10 miles south of downtown Boston was surrounded by oak forest. Detailed hydrocarbon analysis of ambient air samples showed concentrations of isoprene ranging from less than 0.5 ppbC during the night to an average value of 10 ppbC during midday. Occasionally as high as 30 ppbC isoprene were observed. Air samples collected by aircraft over the Boston area also contained isoprene which ranged from less than 0.5 ppbC to 3.5 ppbC (9).

Monoterpenes have been measured by Holdren, Westberg, and Zimmerman (76) in coniferous forests of North Central Idaho using gas chromatographic-mass spectrometric techniques. A total terpene concentration within the forest canopy of between 0.5 to 16 ppbC was reported over 10 month sampling period. Outside of the forest canopy, terpenes could not be detected with a detection limit of less than 0.1 ppbC. Total non-methane hydrocarbon measurements were not made in this study.

In a joint EPA-Duke University study to measure α-pinene fluxes of a loblolly pine forest in North Carolina, over 300 ambient air samples were analyzed (77). Analysis of air samples collected within a few meters above the forest canopy crown showed a range of α-pinene concentration of 0.6 to 13 ppbC during midday. In other experiments at the same location 3 hour integrated samples were collected over 24 hour periods. Simultaneously samples were collected 5 meters above the canopy the other at the base of the canopy. The results of these studies are plotted in Figures 18 and 19. The figures serve to illustrate two important factors. First the terpene concentrations are substantially lower during the winter months probably due to lower volatilization rates at lower temperatures. Secondly noctural inversions serve to contain the terpenes as evidence by the concentration differential between above and below the canopy. In Figure 19 looking at the data of August 23 the 56 ppbC terpenes concentration represents a substantial contribution to the TNMHC of 40% in the canopy. Measurements

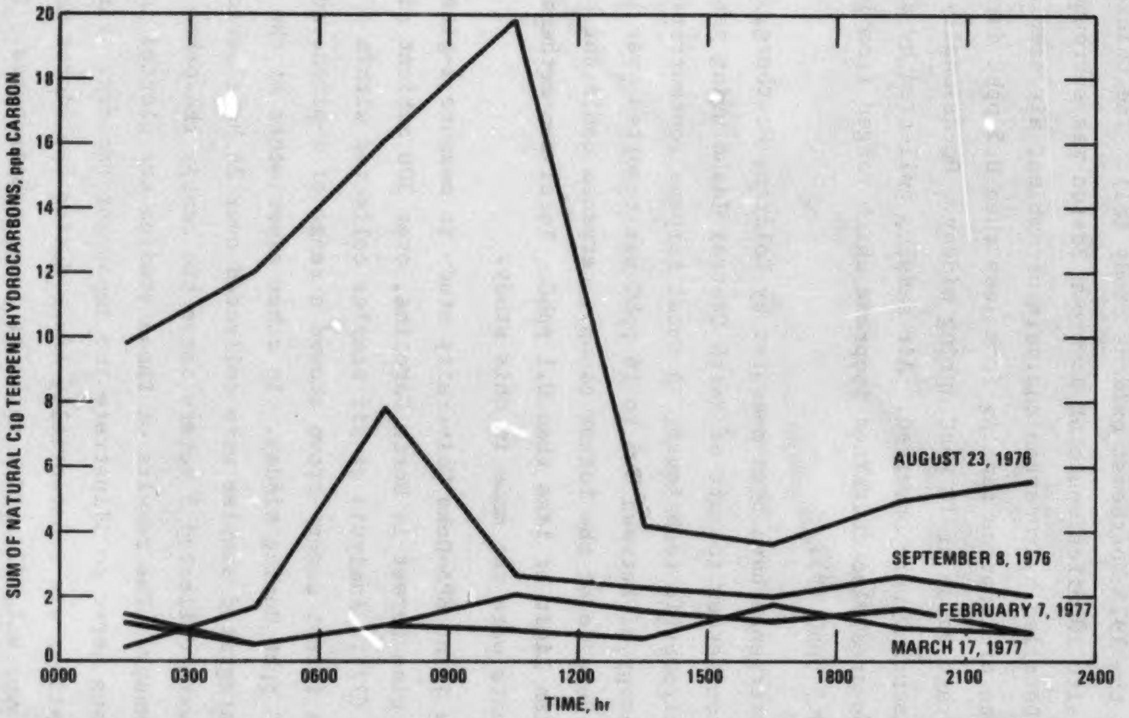


Figure 18. Total concentration of the C_{10} terpene hydrocarbons (ppb carbon) observed above the canopy at the IBP site at different times of the year.

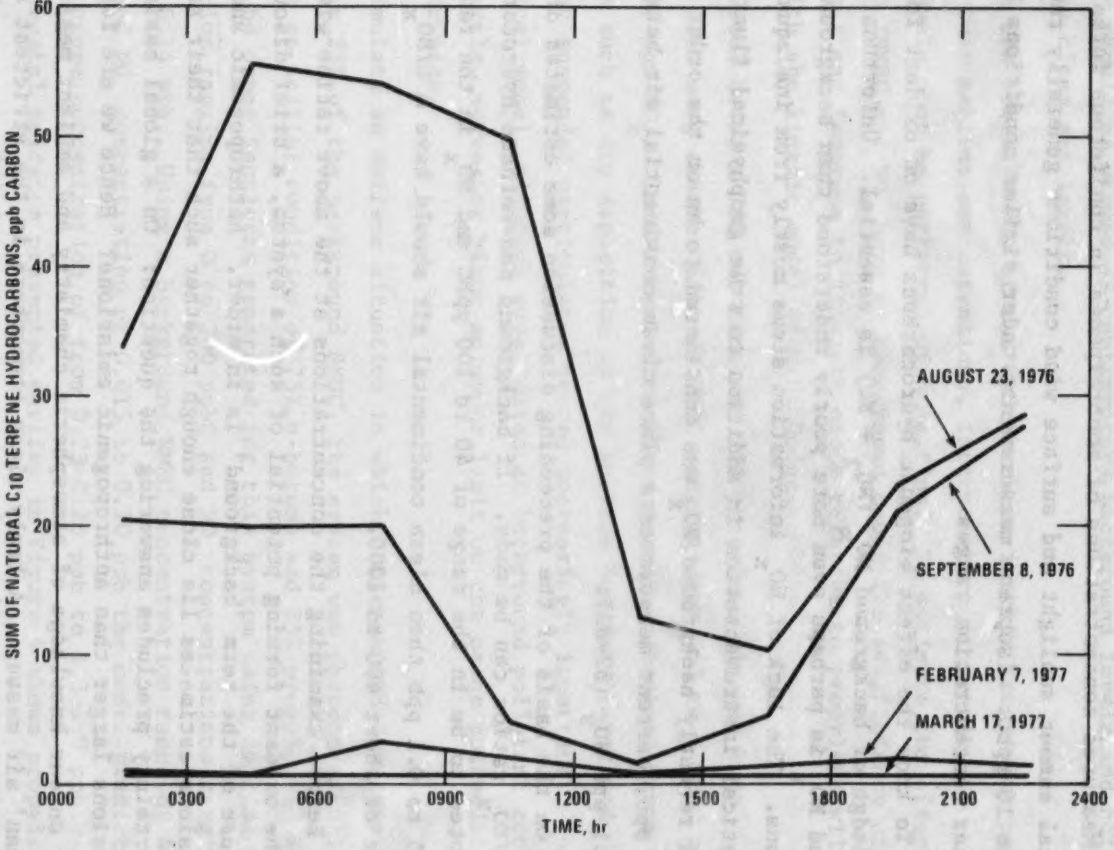


Figure 19. Total concentration of the C_{10} terpene hydrocarbons (ppb carbon) observed in the canopy at the IBP site at different times of the year.

5 meters above the canopy Figure 18 (August 23) resulted in terpenes concentrations accounting for only 12% of the TNMHC. During the early morning periods which are most conducive to biogenic hydrocarbon buildup in the surface boundary layer, the dissipation of the layer promotes mixing and the concentrations decrease.

Measured concentrations of monoterpenes in coniferous forests under typical summer sunlight and surface wind conditions generally range from 0.5 to 10 ppbC. Isoprene measurements under similar conditions have shown similar concentration ranges.

To know the effect biogenic hydrocarbons have on oxidant formation, a knowledge of background NO_x (NO_2 + NO) is essential. Unfortunately background NO_x is perhaps even more poorly understood than background hydrocarbons. The lack of NO_x information stems mostly from inadequate analytical instrumentation in addition to true geophysical fluctuations. Until recently background NO_x was considered to be on the order of 0.5 to 2 ppb, current measurements place clean continential air between 0.015 to 0.1 ppb NO_x (82-83).

On the basis of the preceeding discussion some estimates of background $NMHC/NO_x$ ratios can be made. If background non-methane hydrocarbon is accepted to be in the range of 40 to 100 ppbC and NO_x in the range of 0.015 to 0.1 ppb then clean continental air should have a C/NO_x ratio range of about 400 to 7000.

Before examining the concentrations at the above ratios with respect to the oxidant forming potential of such a system, a brief discussion of the use of the term 'background' is in order. Anthropogenic and biogenic emissions estimates lie close enough together such that their range of uncertainty precludes answering the question: On a global basis are biogenic emissions larger than anthropogenic emissions? Hence we are forced to rely on our knowledge of atmospheric chemistry and ambient measurements in 'clean' air masses. A truly clean atmosphere in the strictest sense described as air unaffected by man's activities no longer exists. Since the advent of the Industrial Revolution, large scale burning of fossil fuels and the manufacture of synthetic chemicals has introduced pollutants into the atmosphere. The cleanest air today is recognized by the lowest measured levels of distinctly anthropogenic origin and preferably tropospherically inert compounds i.e. acetylene, CCl_3F. The background values for TNMHC and NO_x cited earlier reflect the lowest levels measured in a well mixed air mass not necessarily free from man's influence. The values should be viewed as contemporary background levels and not necessarily clean air levels.

Since the irradiations of the hydrocarbons in this study were performed at higher than ambient concentrations, interpolation of results to ambient levels must be performed with caution. To estimate the effects background TNMHC and NO_x have on background ozone the inefficiency of the terpenes and isoprene to generate ozone relative to propylene will be coupled with the kinetic model of M.C. Dodge.

The model using a 75% n-butane and 25% propylene mix has been validated with smog chamber data at NMHC ranging from 0.2 to 5 ppmC and 0.05 to 0.6 ppm NO_x. In the real atmosphere poorly understood ozone removal mechanisms such as dry deposition at the surface boundary layer and destruction by suspended particulates become increasingly important. The photochemical model, although unvalidated at background pollutant concentration levels, serves to place an upper limit on the ozone potential of such an air mass.

To simulate an extreme situation in which terpenes and isoprene contributed to 25% of the background NMHC, the system was photochemically modeled at an initial condition of 75% n-butane and 25% propylene. Figure 20 shows the ozone isopleths generated for this system using initial NMHC concentration ranging from 0 to 200 ppbC and NO_x concentrations ranging from 0 to 0.14 ppb. Using a background NMHC concentration range of 40 to 100 ppbC and NO_x concentration of 0.015 to 0.10 ppb the model predicts a maximum ozone concentration of from 0.23-0.26 ppb to 1.3-1.9 ppb. Since the experimental evidence presented earlier in Figure 4 shows propylene to be four times more efficient than isoprene and nearly ten times more efficient than α-pinene at generating ozone from the same quantity of NO_x then the photochemical model estimates which uses propylene are even more

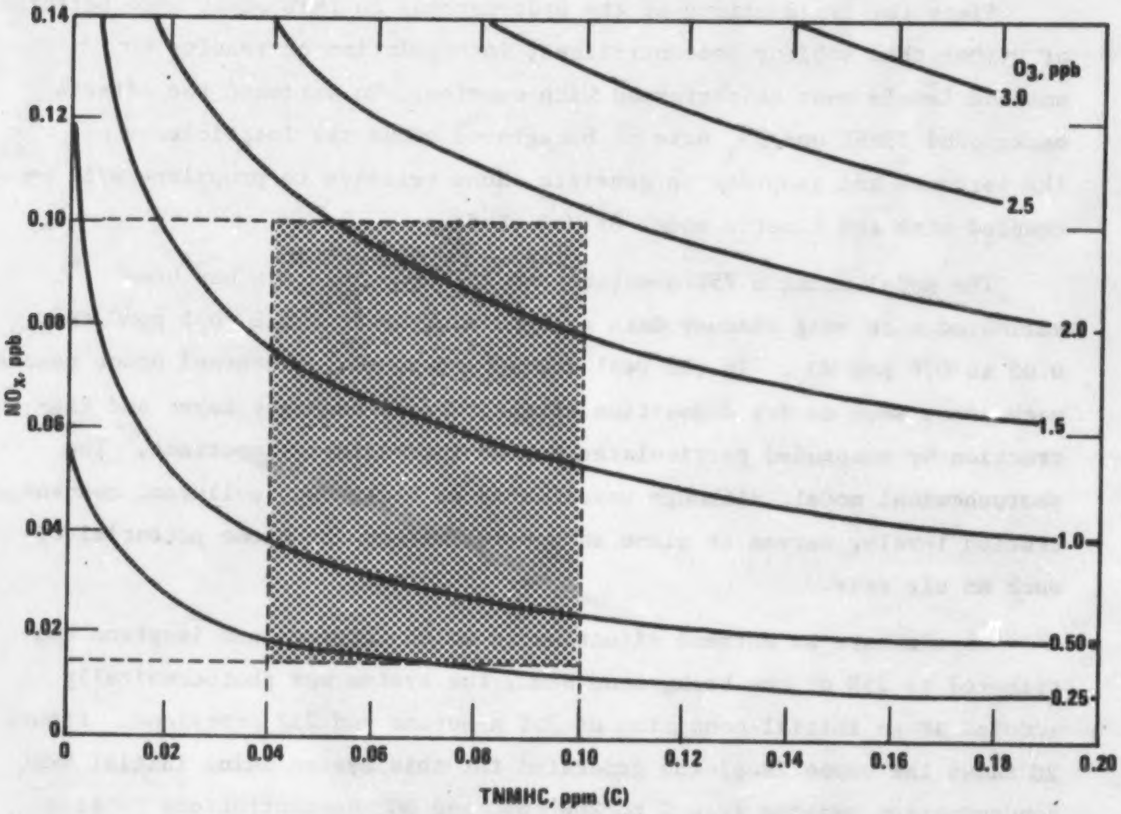


Figure 20. Ozone isopleths predicted from Dodge's photochemical model (75 percent n-butane/25 percent propylene).

overpredictive for these compounds.

In summary the experiments that have been conducted and reported in this report do not support the hypothesis that terpenes and isoprene contribute significantly to the 30-40 ppb geophysical ozone concentration. The biogenic hydrocarbons and oxides of nitrogen are simply not present in high enough concentrations and at the proper proportions to generate much photochemical ozone.

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APPENDIX A

Determination of Ozone-Isoprene Rate Constant

A review of recent kinetic rate constant literature reveals the ozone-isoprene rate constant has not been reported. The measurement of this rate constant is important since isoprene and ozone co-exist in the atmosphere, hence their rate of reaction is of importance to better understanding the atmospheric chemistry of isoprene. A study was undertaken to determine experimentally the reaction rate constant for the ozone-isoprene reaction

The ozone-isoprene dark reactions were conducted in 130 X 110 cm heat-sealed 2-mil FEP Type A Teflon film bags. The Teflon bag was first filled with 330 liters of purified air containing less than 2 ppb NO_x and less than 50 ppb non-methane hydrocarbon comprised mostly of ethane and propane. A calculated amount of isoprene (99% purity) was injected into the purified air stream with a calibrated microliter liquid syringe which had been cooled to deliver a true liquid sample. After the addition of isoprene, ozone was introduced into the isoprene-air mixture by passing the air stream filling the bag through a high voltage discharge ozonator.

Ozone decay in the Teflon bag in the absence of isoprene was less than 1% per hour. Ozone was monitored intermittently over the 45-minute period of the experiments with a Bendix Model 8002 ozone-ethylene chemiluminescence instrument. This instrument was modified to measure up to 10 ppm full scale. The signal output was logged by an Esterline Angus (Model D-2020) printing digital volt meter.

Isoprene decay in the bag in the absence of ozone was negligible during the time-frame of these experiments. Isoprene was measured with a Perkin-Elmer 900 gas chromatograph with flame ionization detection. The sample was drawn directly from the bag through a gas-sampling loop and injected via a solenoid-actuated Seiscor sampling valve. Separation was achieved with a 0.45 m X 3 mm o.d. stainless steel column containing 60-80 mesh Porapak Q and maintained at

100°C. The GC output was interfaced to a Perkin-Elmer PEP-1 data system for peak integration.

For comparative purposes propylene was reacted with ozone to determine its rate constant. The results of the propylene and isoprene experiments are presented in Table 1-A.

TABLE 1-A. REACTION OF OZONE WITH ISOPRENE AND PROPYLENE

Experimental Data - Reaction at 22 ± 1°C, 45 minutes

	Initial Hydrocarbon Conc. (PPM)	Initial Ozone Conc. (PPM)	Ratio Initial Hydrocarbon to ozone	Ratio Decrease in Hydrocarbon Conc. to Decrease in ozone conc.
Isoprene	6.84	0.45	15.1	0.93
	0.47	2.29	0.2	0.81
	0.61	4.01	0.2	0.65
Propylene	1.60	1.93	0.8	1.13
	5.24	1.12	4.7	1.17
	5.61	0.71	7.7	1.19
	8.65	0.31	27.6	1.18

In the case of isoprene more ozone than isoprene is being consumed. The stoichiometry of the reaction is nearer to 1:1 when isoprene is in excess and the reaction non-stoichiometric when ozone is in excess. This phenomena is probably due to a second attack by ozone on the remaining double bond of the products methyl vinyl ketone or methacrolein formed in the first ozone reaction. The effect is most pronounced when ozone is in excess. Calculated as a simple bimolecular reaction with 1:1 stoichiometry the isoprene-ozone rate constant is 1.89 X 10^{-2} $\text{ppm}^{-1}\text{min}^{-1}$. This rate is reasonably close to that of the 1,3-butadiene-ozone rate constant reported by Hanst (57) of 1.2 X

10^{-2} ppm^{-1}min^{-1}.

As a check on the experimental methodology, propylene was investigated to compare results with published values. Although the determination of second order rate constant is complicated slightly by competing side reactions a rate of 1.9 X 10^{-2} ppm^{-1} min^{-1} was obtained. This rate agrees extremely well with the rate determined by Japar et al. (55) of 1.92 X 10^{-2} ppm^{-1}min^{-1}. For a more detailed discussion of the propylene-ozone mechanism see Dodge and Arnts (84).

APPENDIX B - INDEX OF FIGURES

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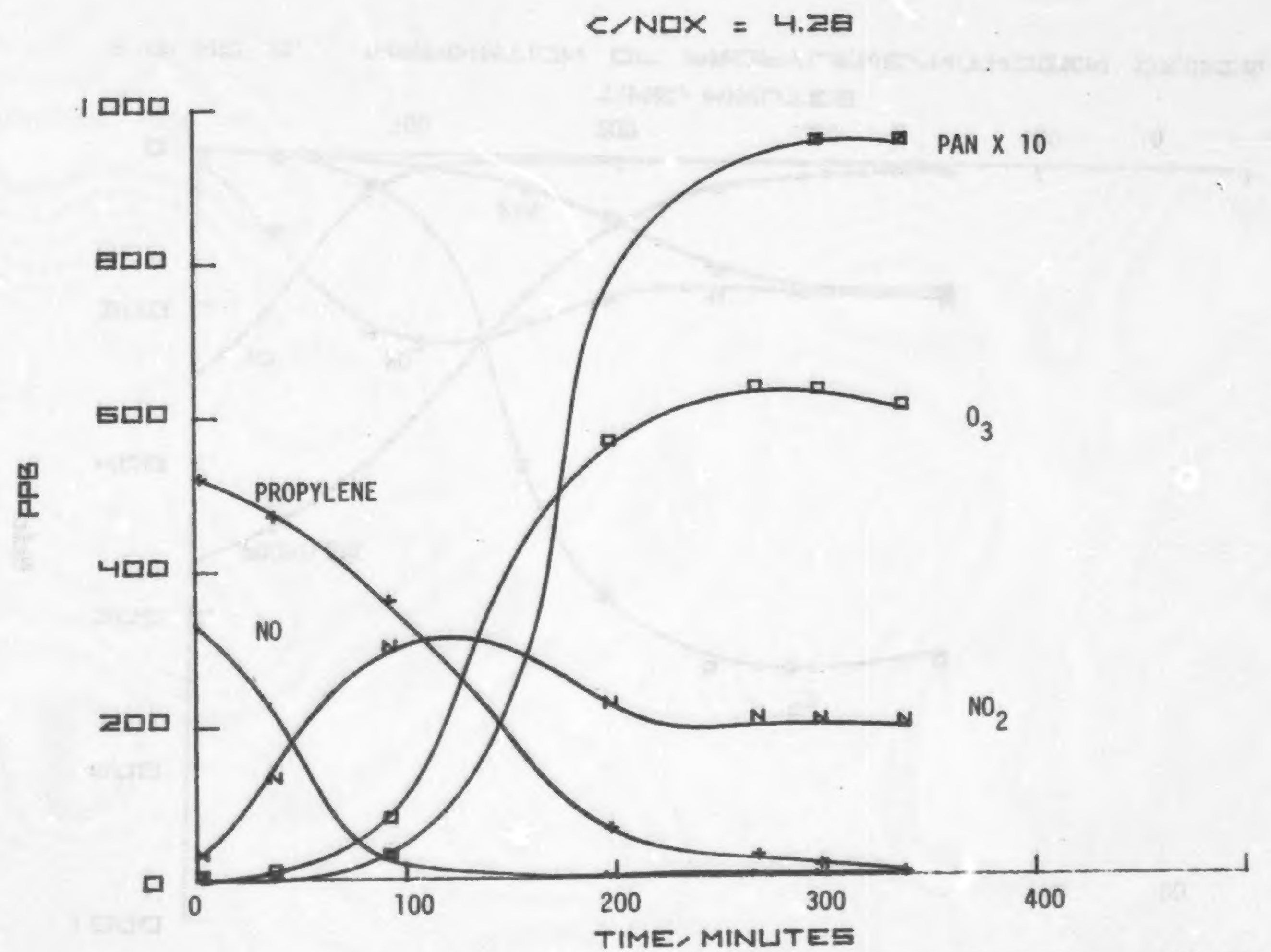


FIGURE 1B. IRRADIATION OF PROPYLENE/NITROGEN OXIDES

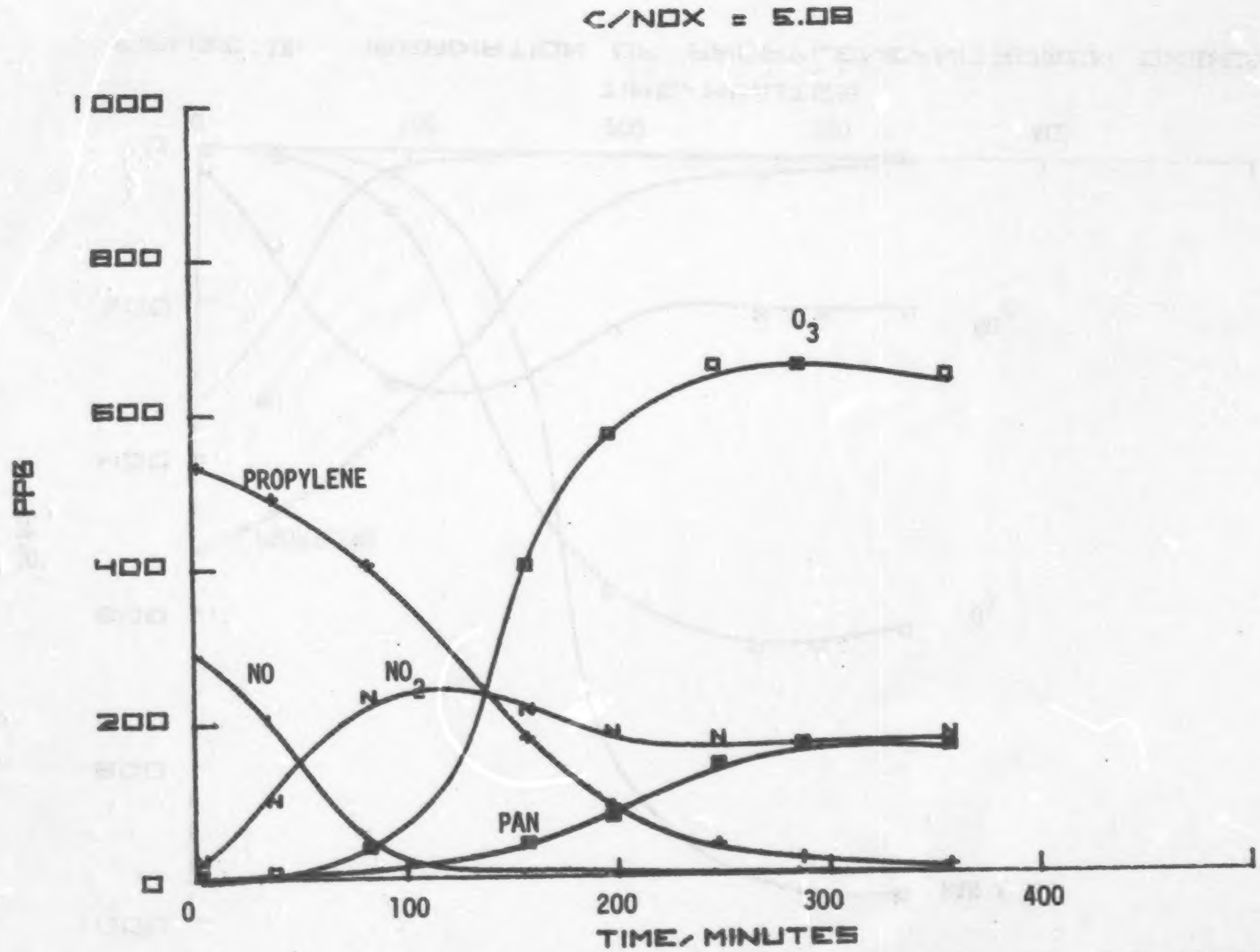


FIGURE 2B. IRRADIATION OF PROPYLENE/NITROGEN OXIDES

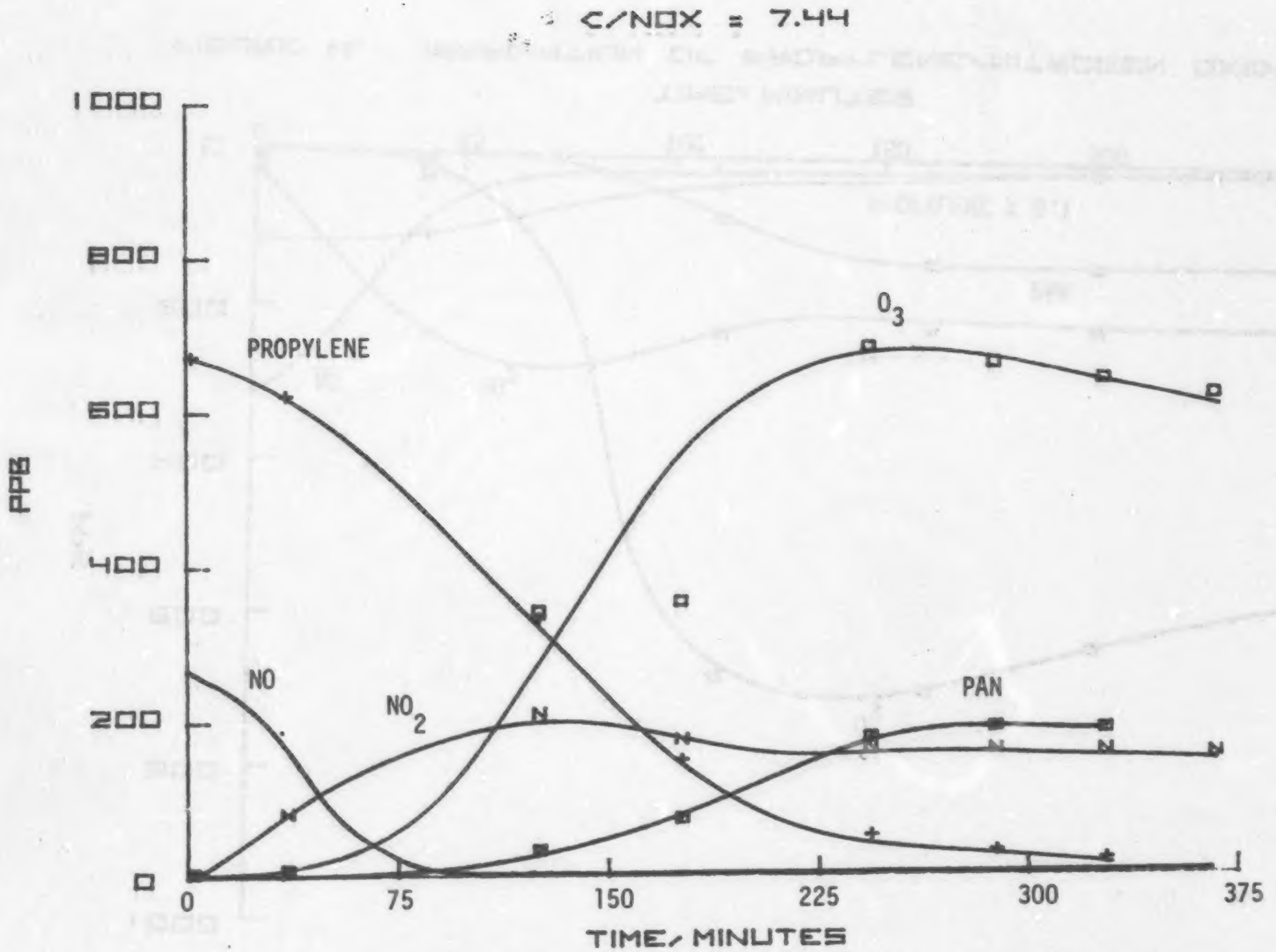


FIGURE 3B. IRRADIATION OF PROPYLENE/NITROGEN OXIDES

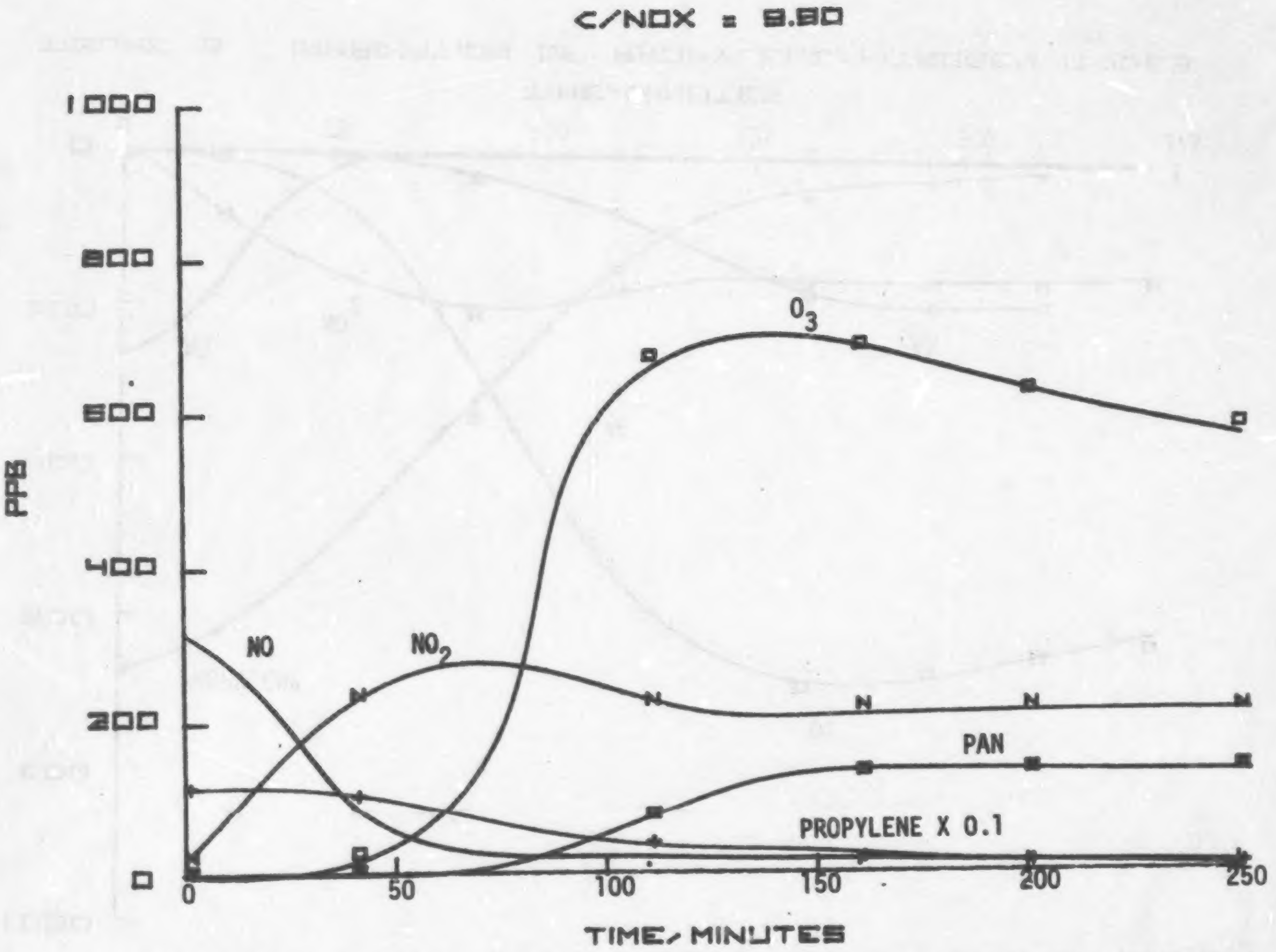


FIGURE 4B. IRRADIATION OF PROPYLENE/NITROGEN OXIDES

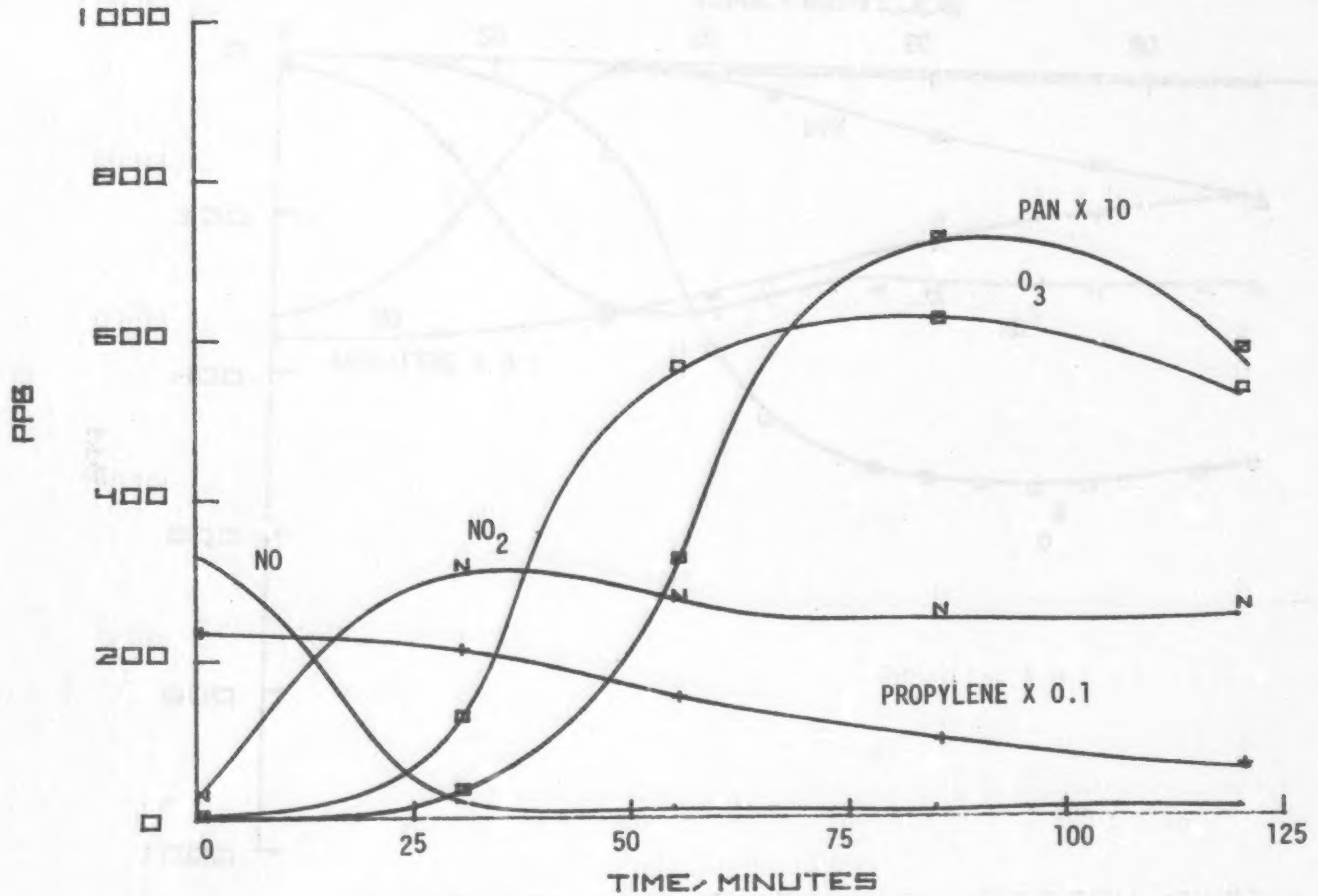
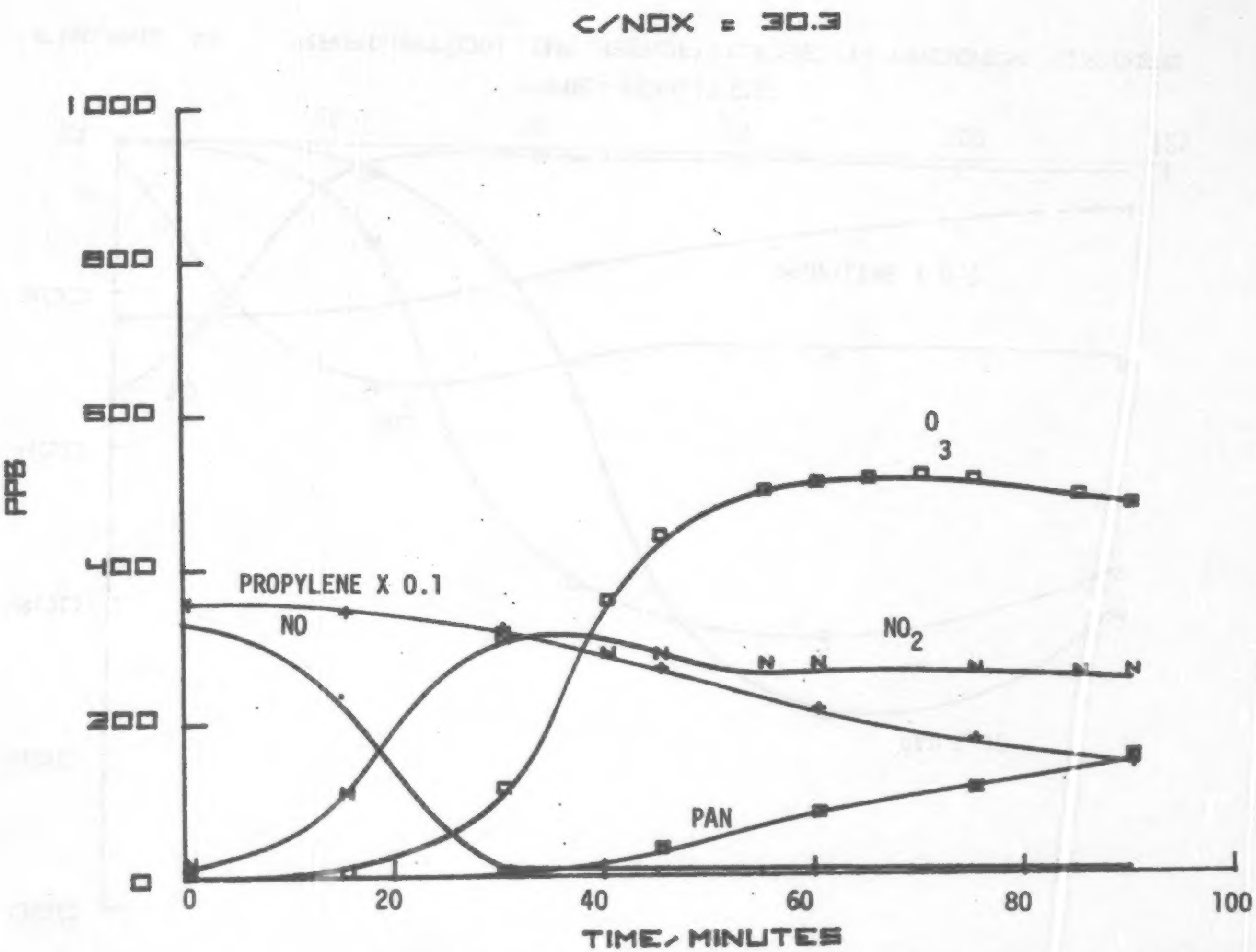

C/NOX = 19.3

FIGURE 5B. IRRADIATION OF PROPYLENE/NITROGEN OXIDES



C/NOX = 30.3

FIGURE 6B. IRRADIATION OF PROPYLENE/NITROGEN OXIDES

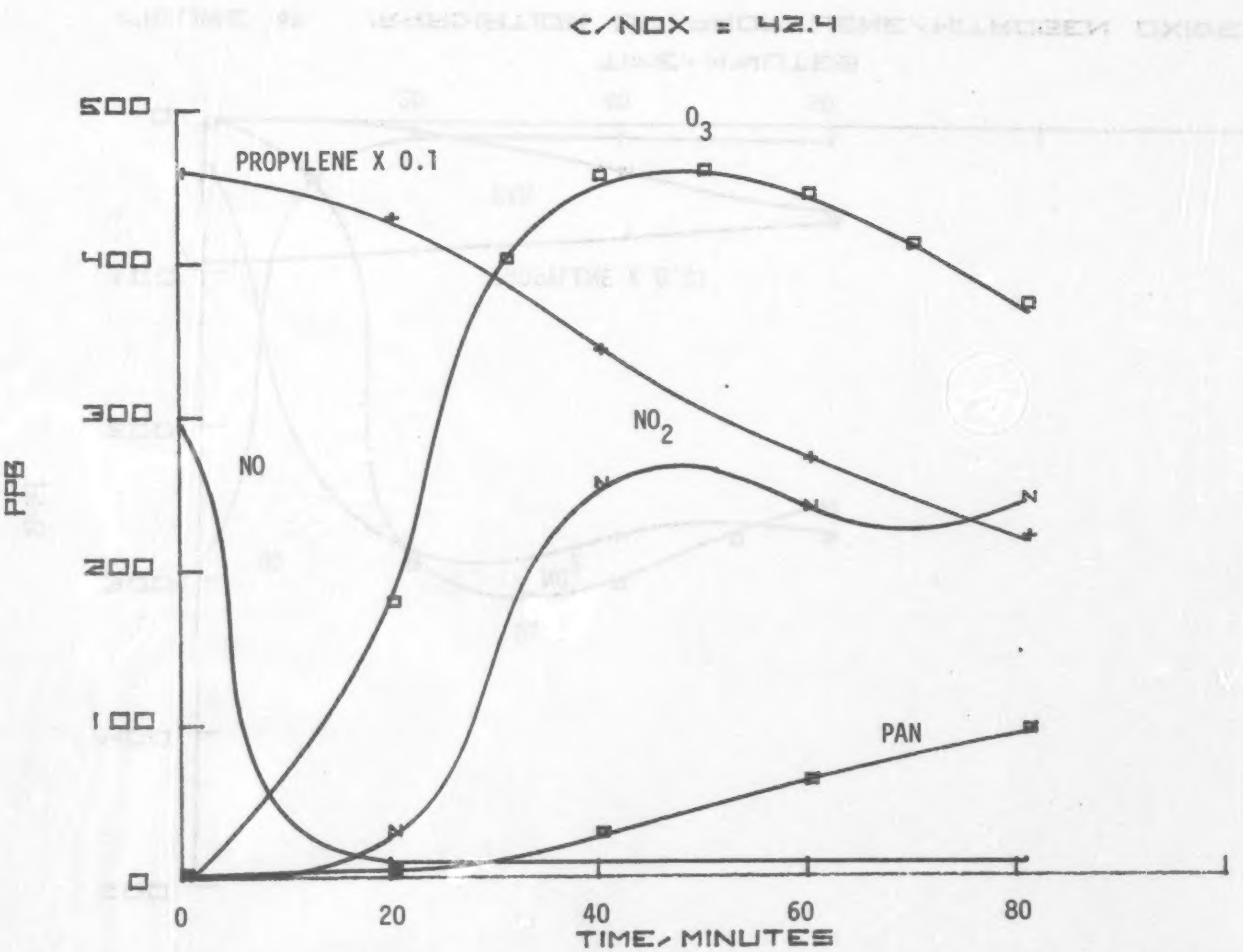


FIGURE 7B. IRRADIATION OF PROPYLENE/NITROGEN OXIDES

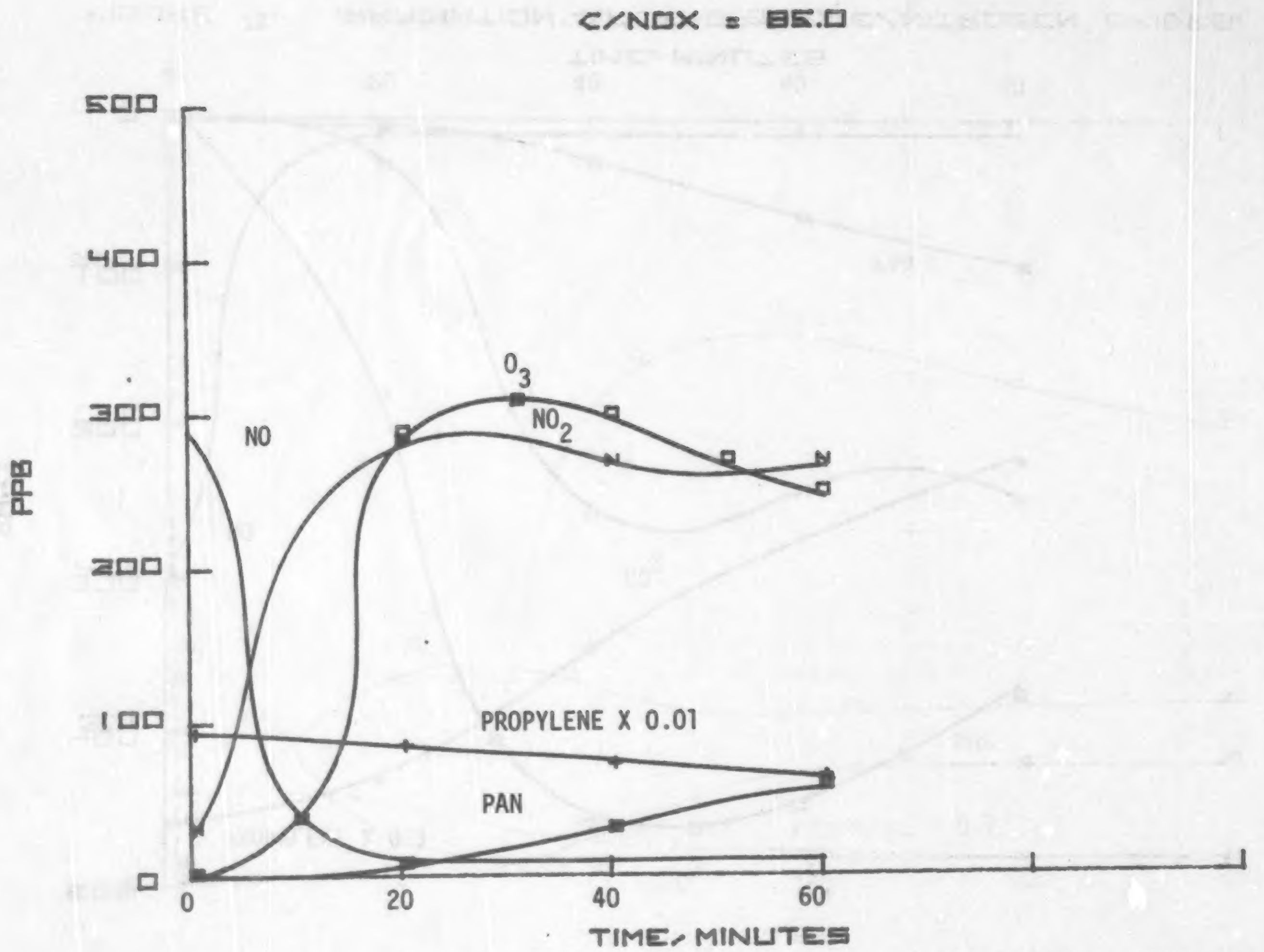


FIGURE 8B. IRRADIATION OF PROPYLENE/NITROGEN OXIDES

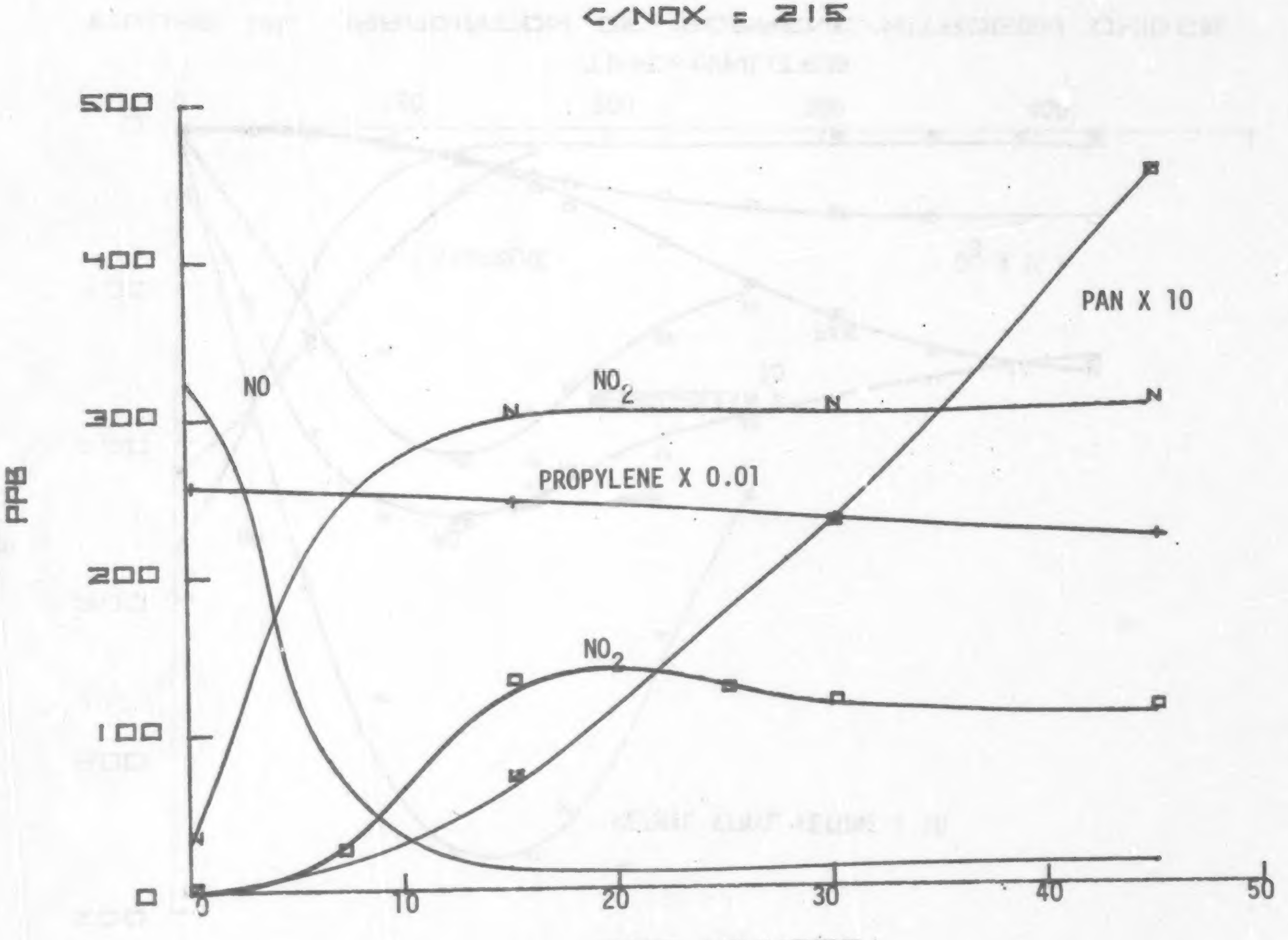


FIGURE 9B. IRRADIATION OF PROPYLENE/NITROGEN OXIDES

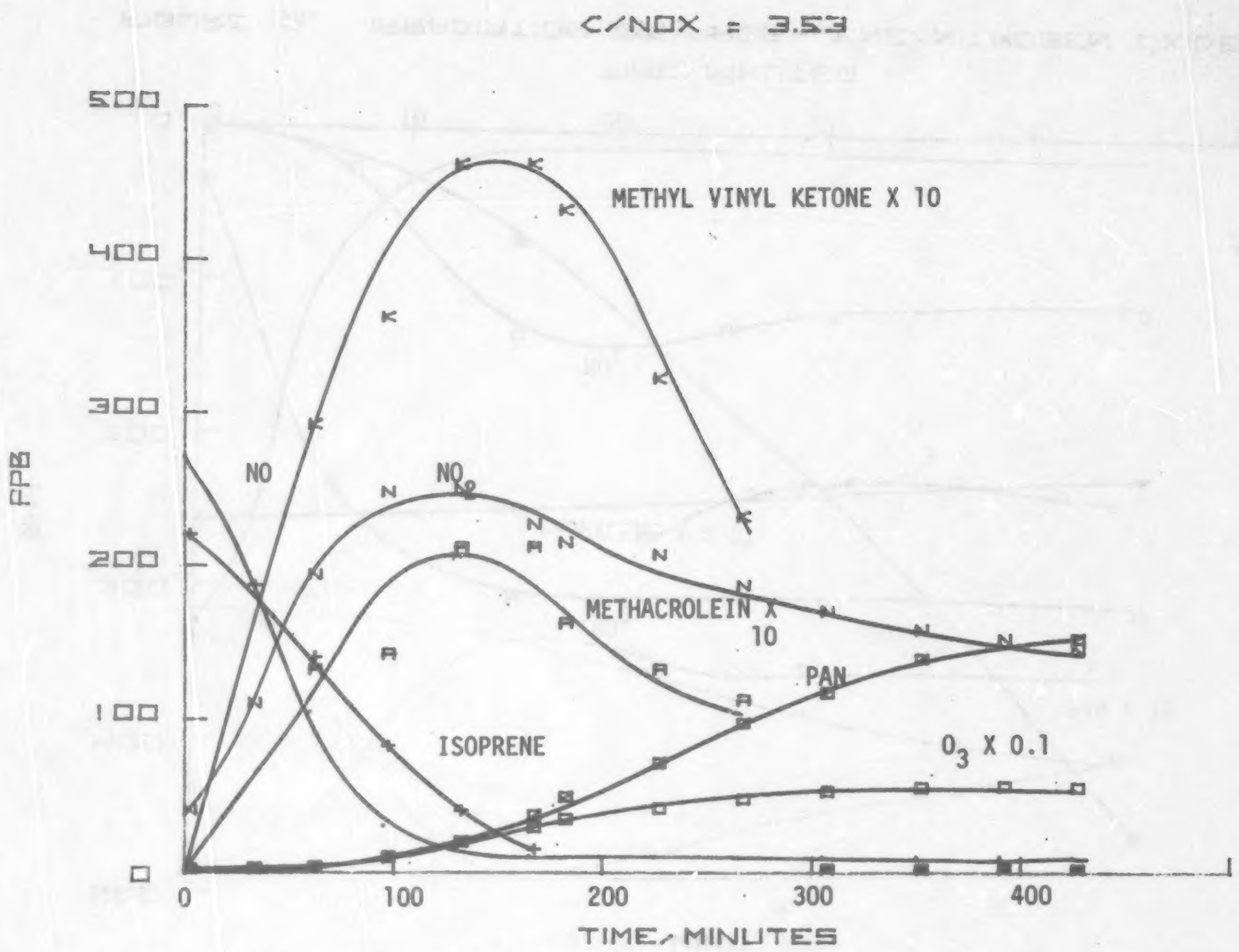


FIGURE 10B. IRRADIATION OF ISOPRENE/NITROGEN OXIDES

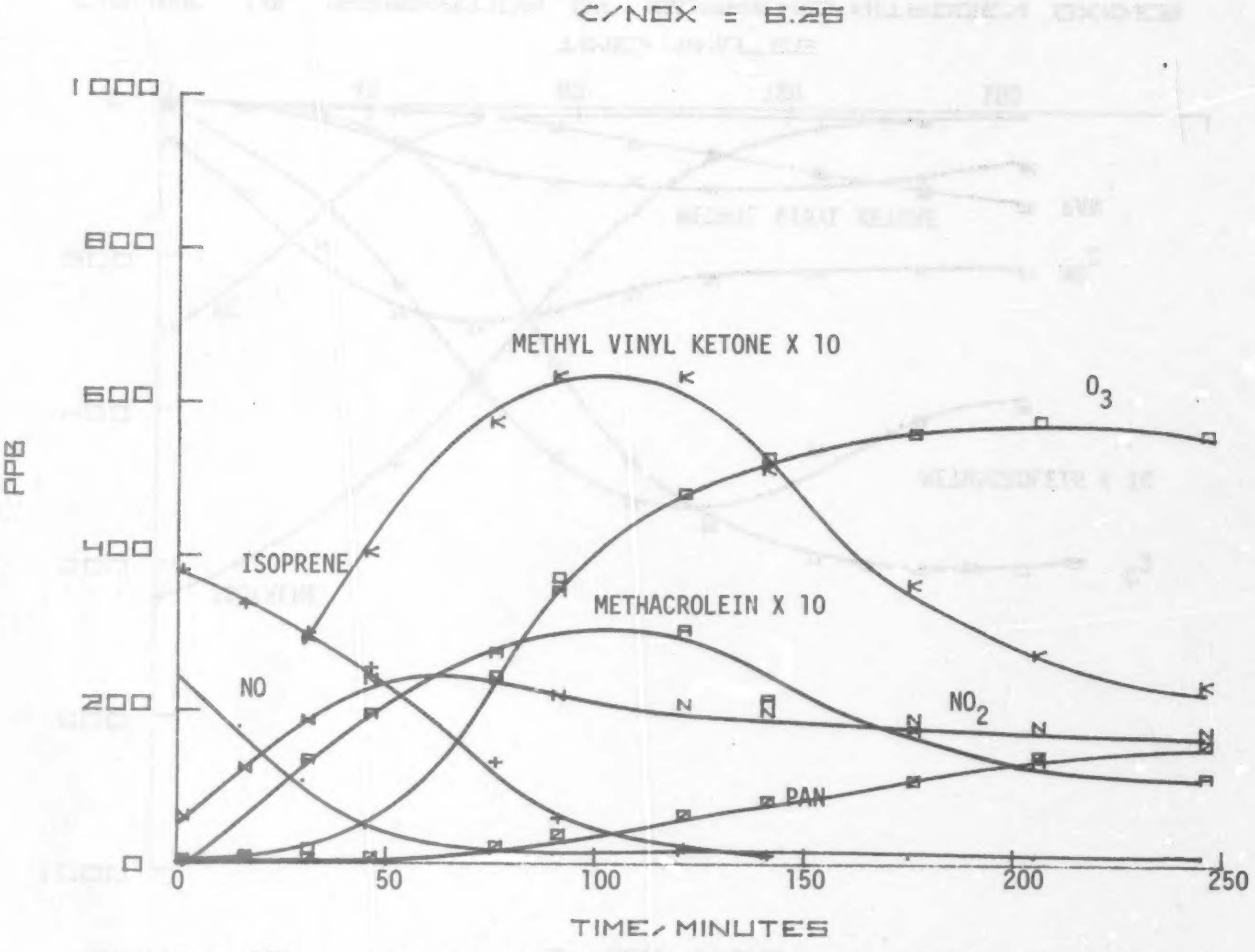


FIGURE 11B. IRRADIATION OF ISOPRENE/NITROGEN OXIDES

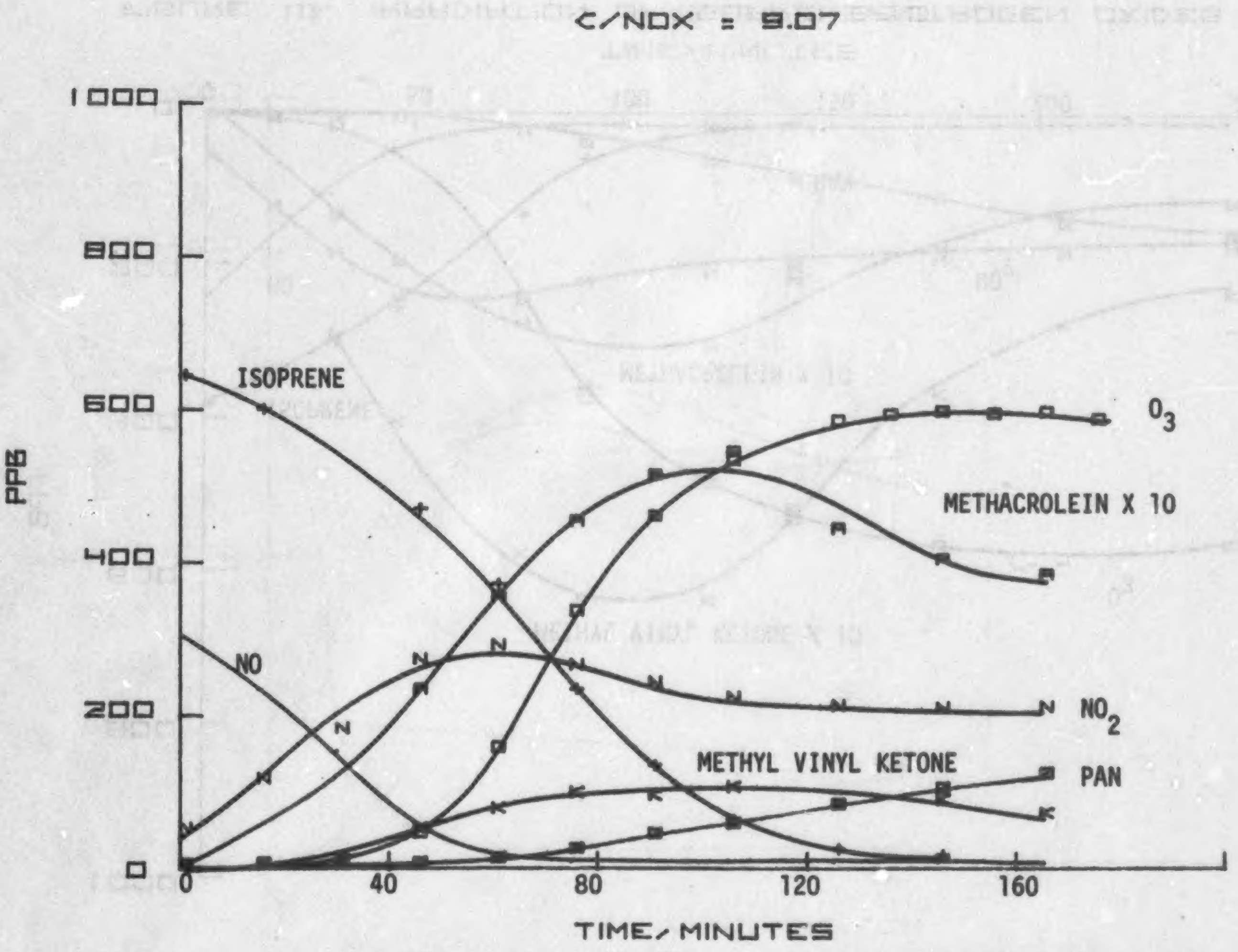


FIGURE 12B. IRRADIATION OF ISOPRENE/NITROGEN OXIDES

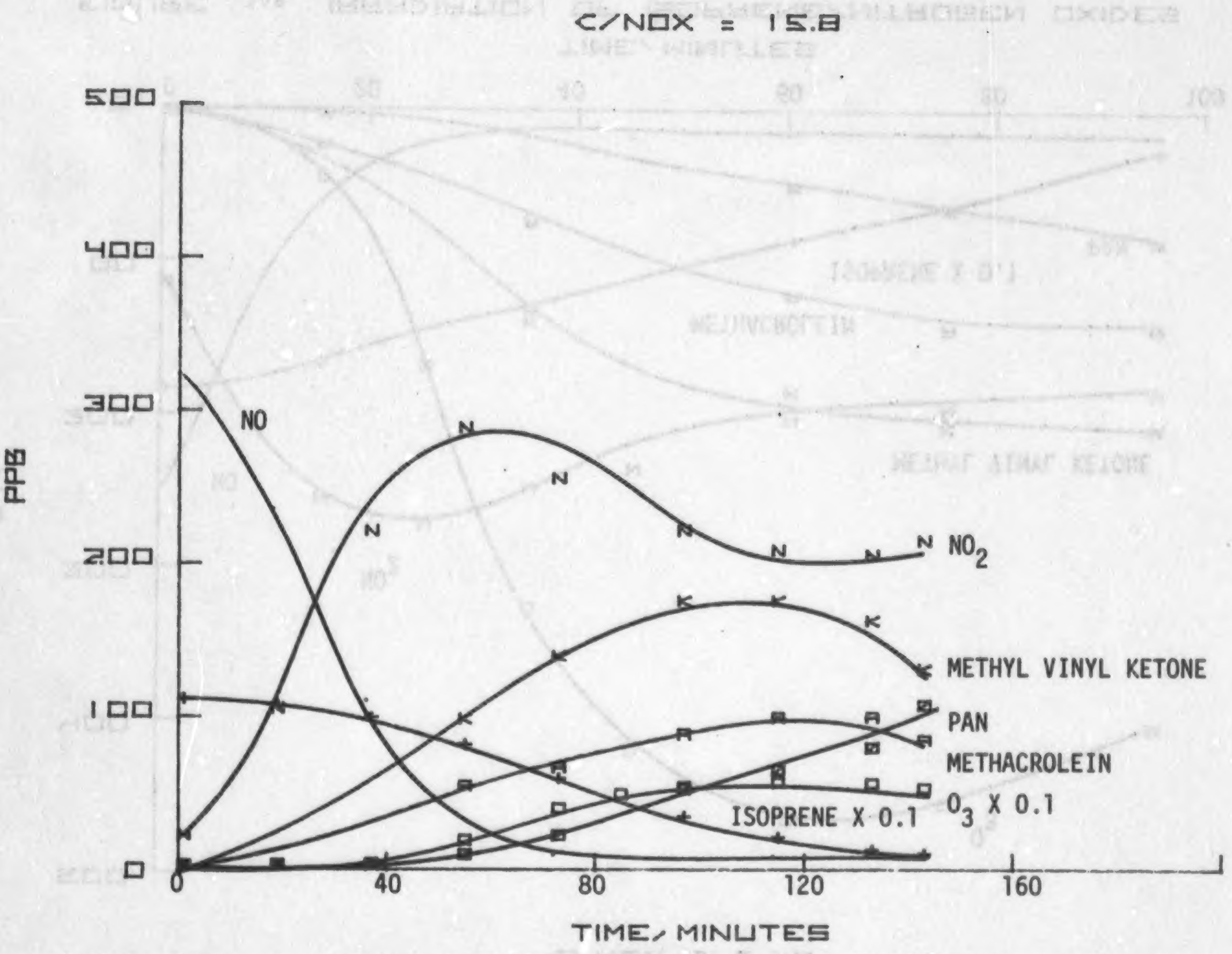


FIGURE 13B. IRRADIATION OF ISOPRENE/NITROGEN OXIDES

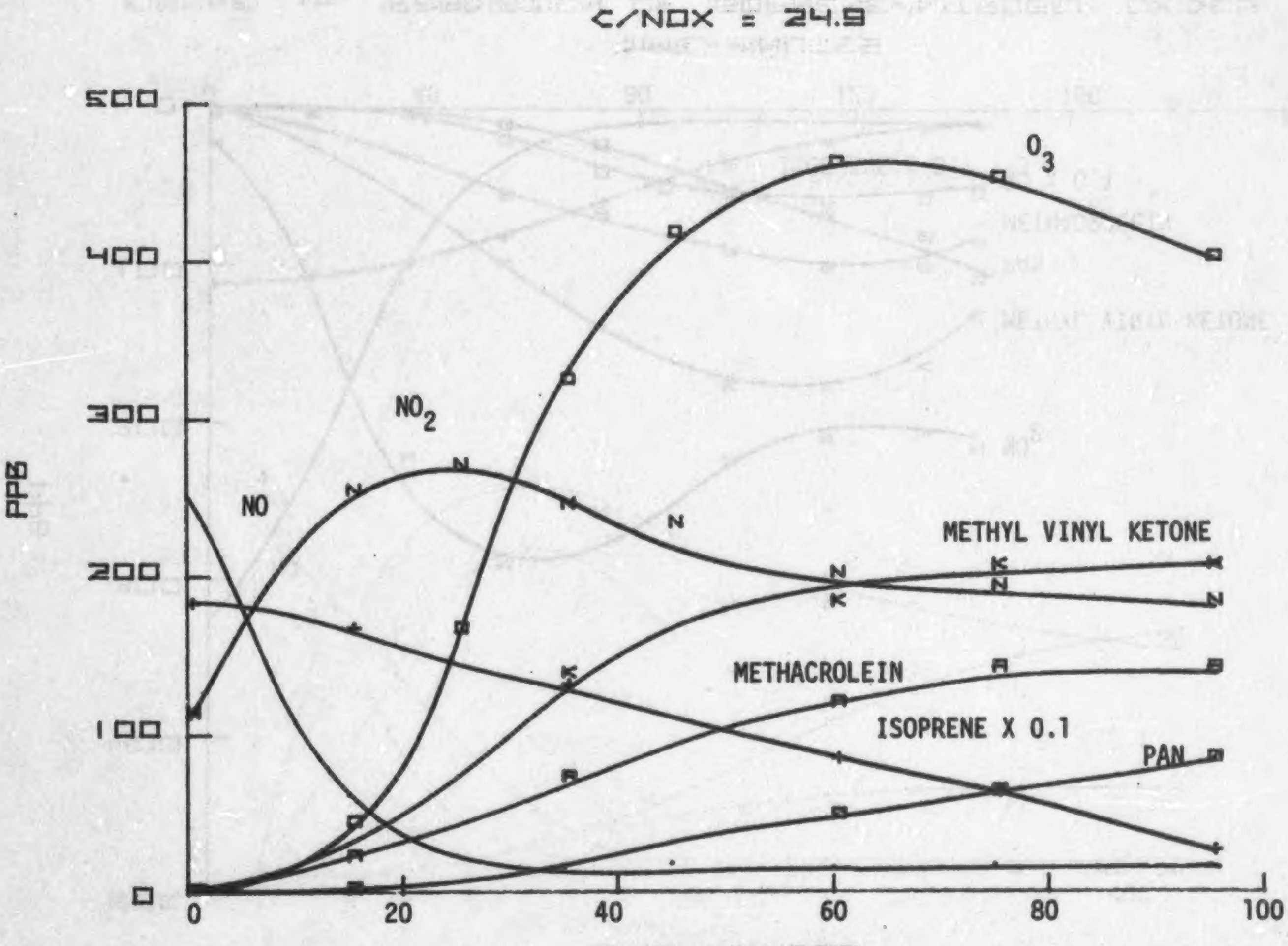


FIGURE 14B. IRRADIATION OF ISOPRENE/NITROGEN OXIDES

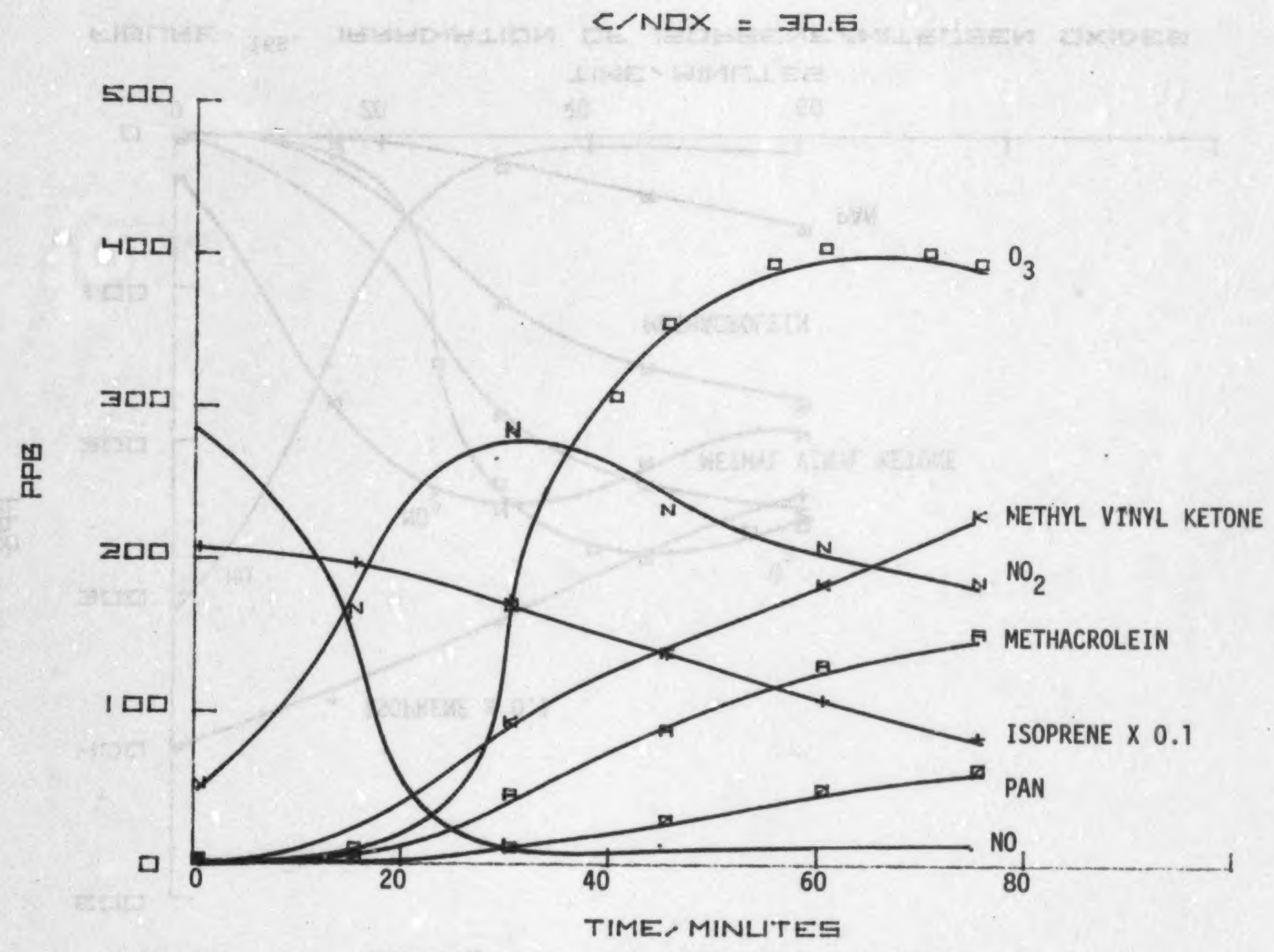


FIGURE 15B. IRRADIATION OF ISOPRENE/NITROGEN OXIDES

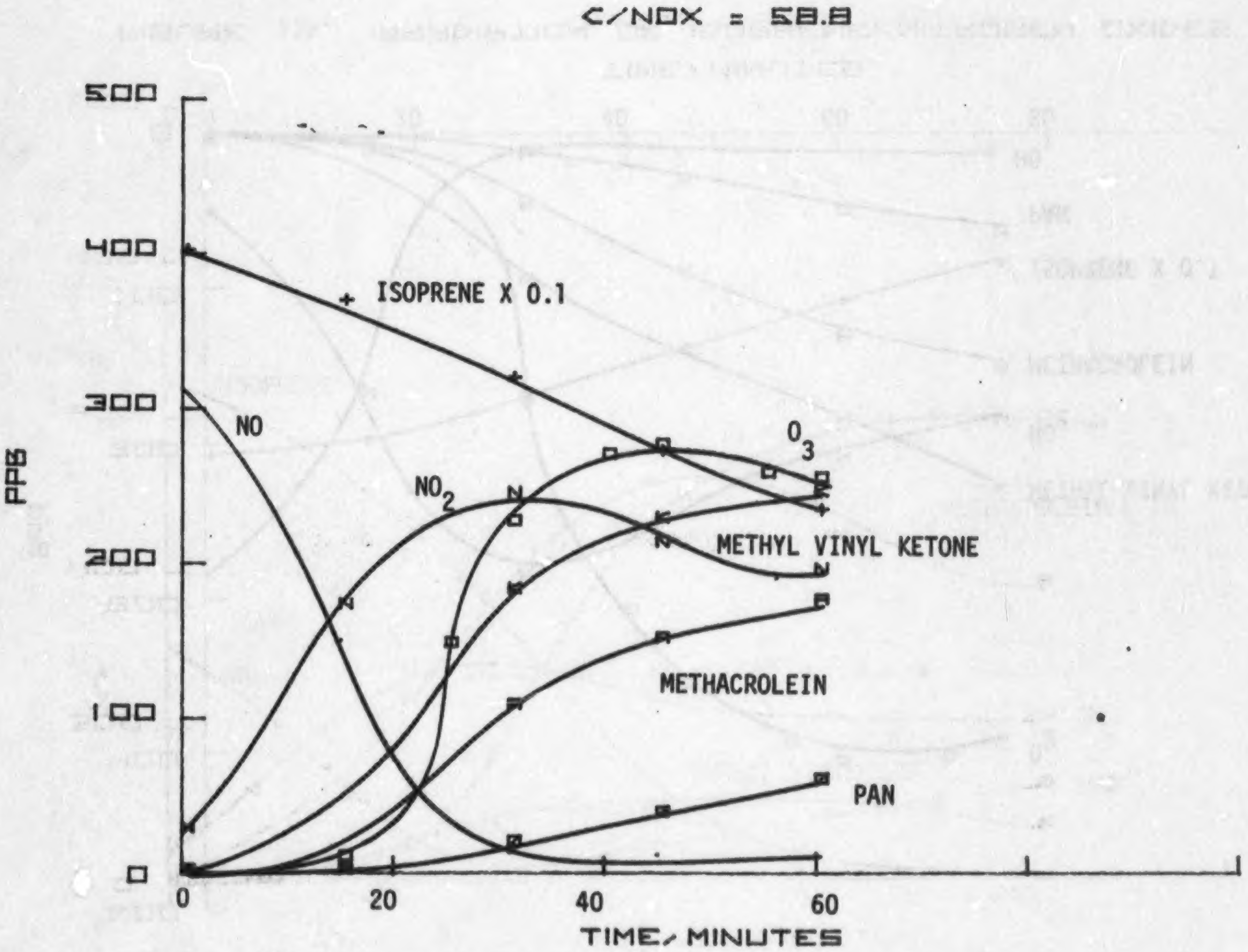


FIGURE 16B. IRRADIATION OF ISOPRENE/NITROGEN OXIDES

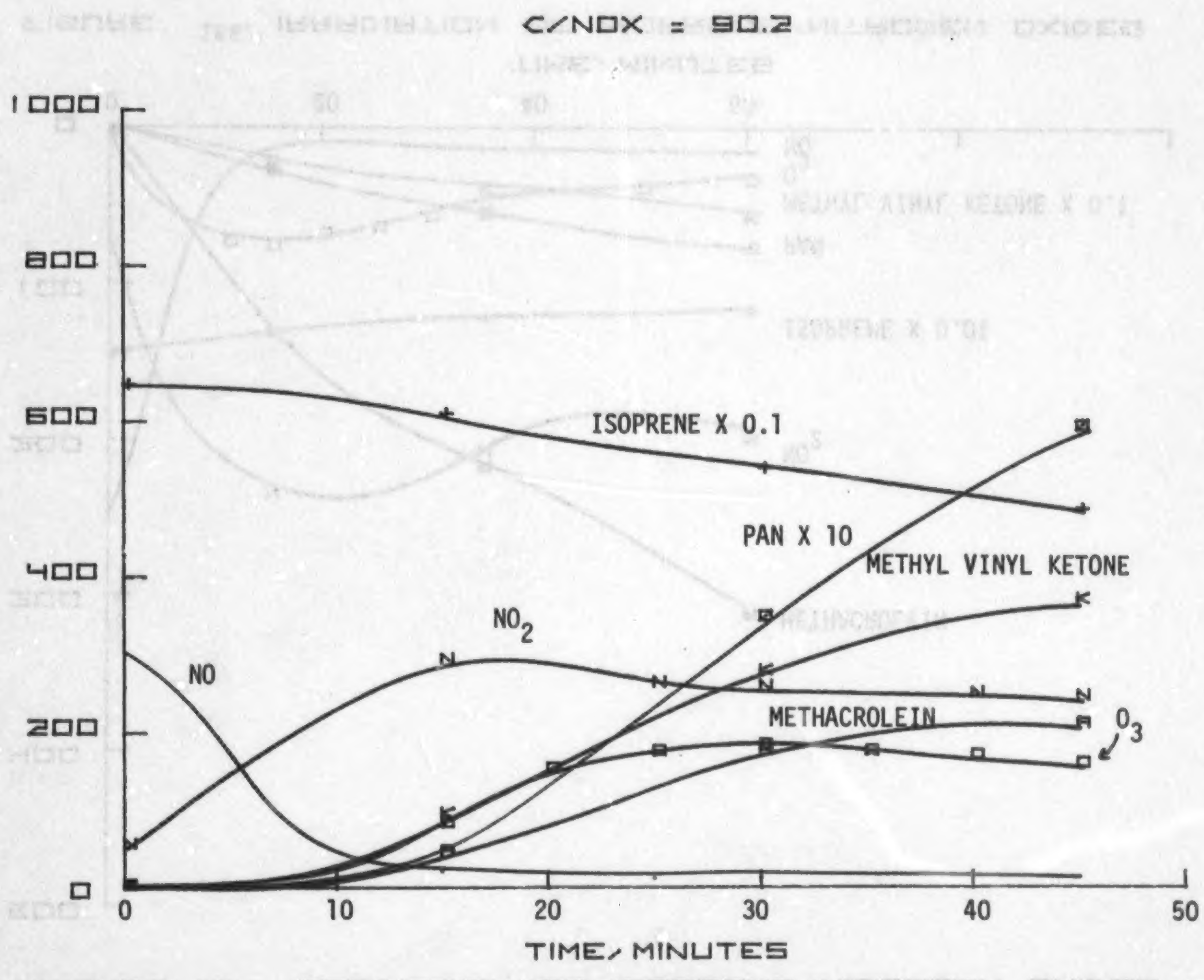


FIGURE 17B. IRRADIATION OF ISOPRENE/NITROGEN OXIDES

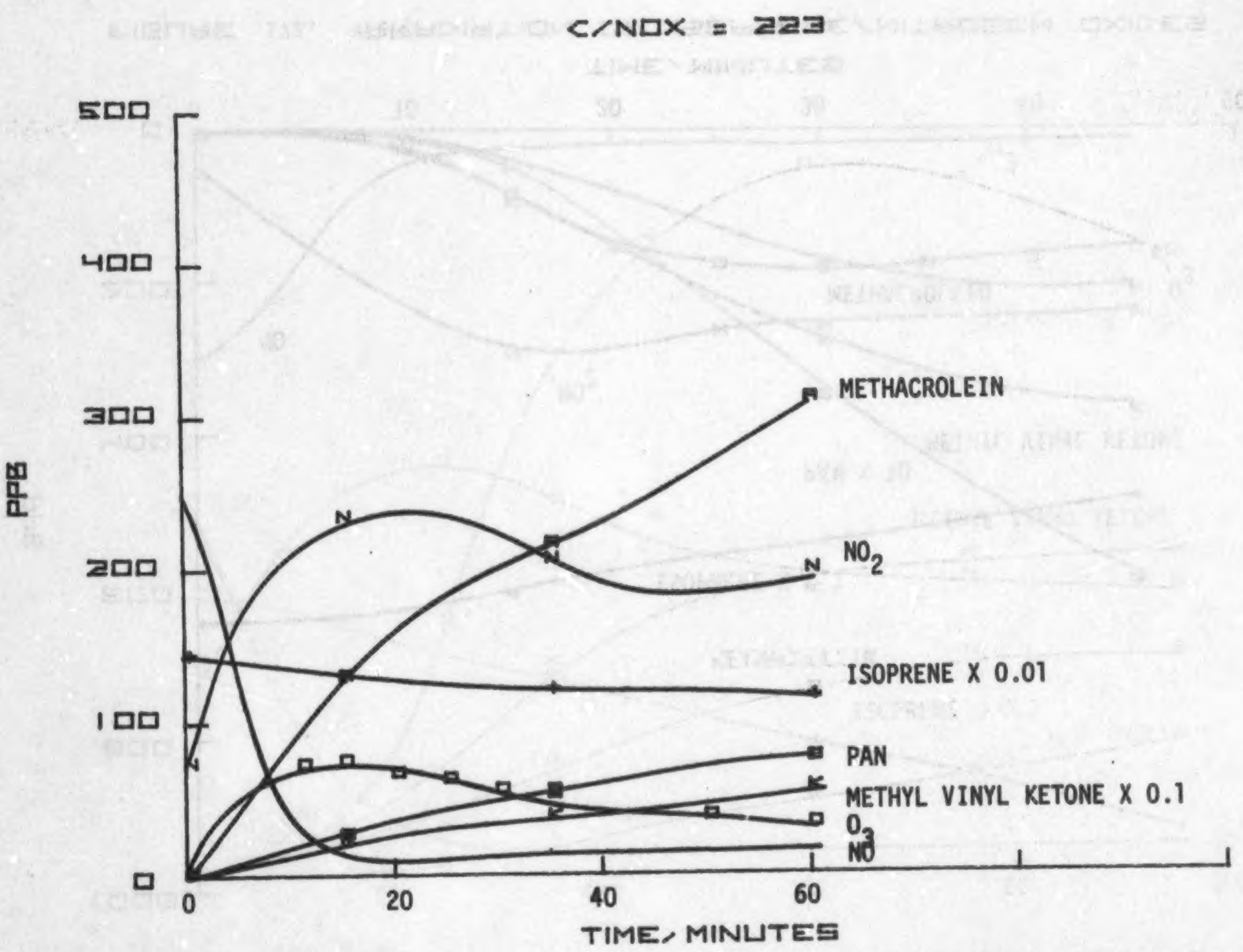


FIGURE 18B. IRRADIATION OF ISOPRENE/NITROGEN OXIDES

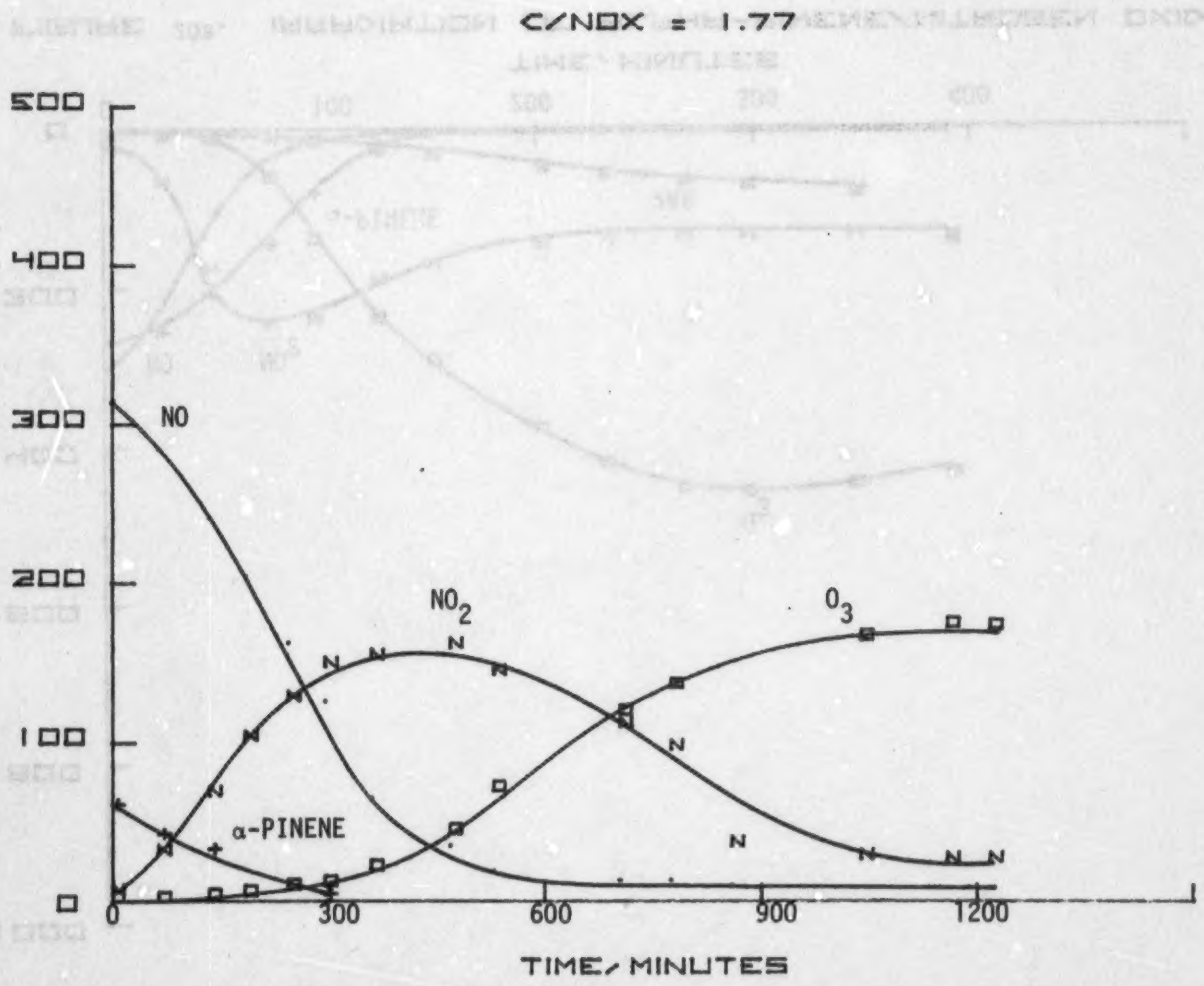


FIGURE 19B. IRRADIATION OF ALPHA-PINENE/NITROGEN OXIDES

C/NOX = 8.1

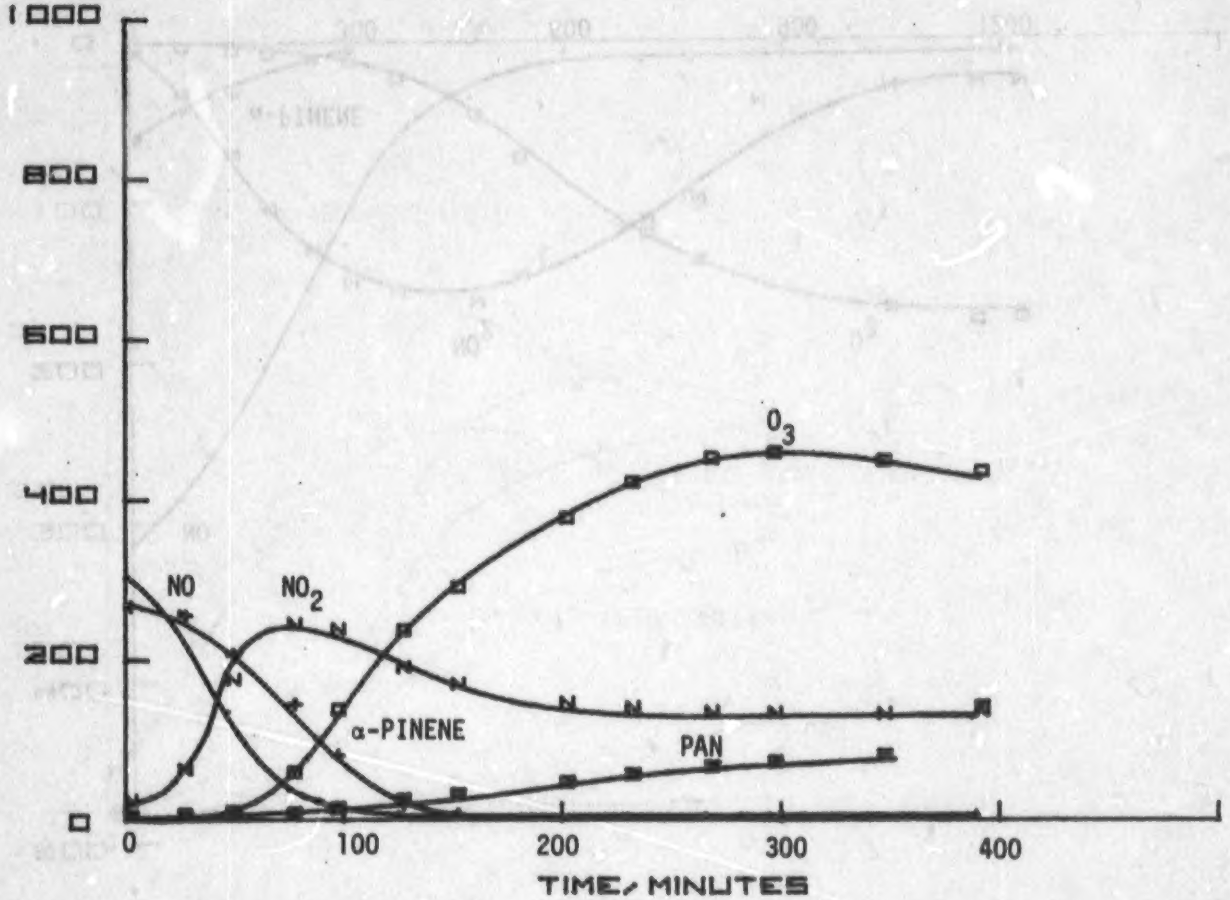


FIGURE 20B. IRRADIATION OF ALPHA-PINENE/NITROGEN OXIDES

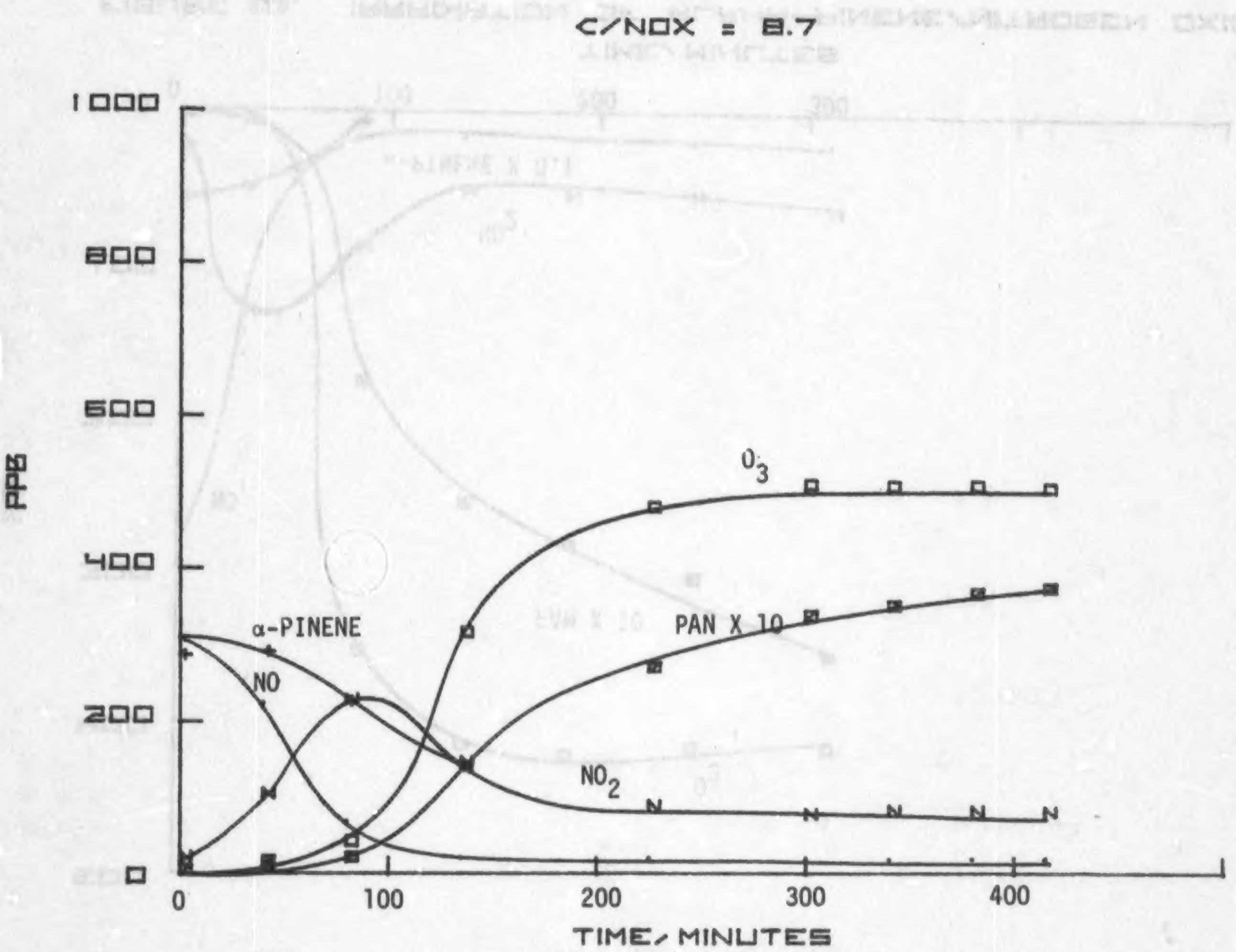


FIGURE 21B. IRRADIATION OF ALPHA-PINENE/NITROGEN OXIDES

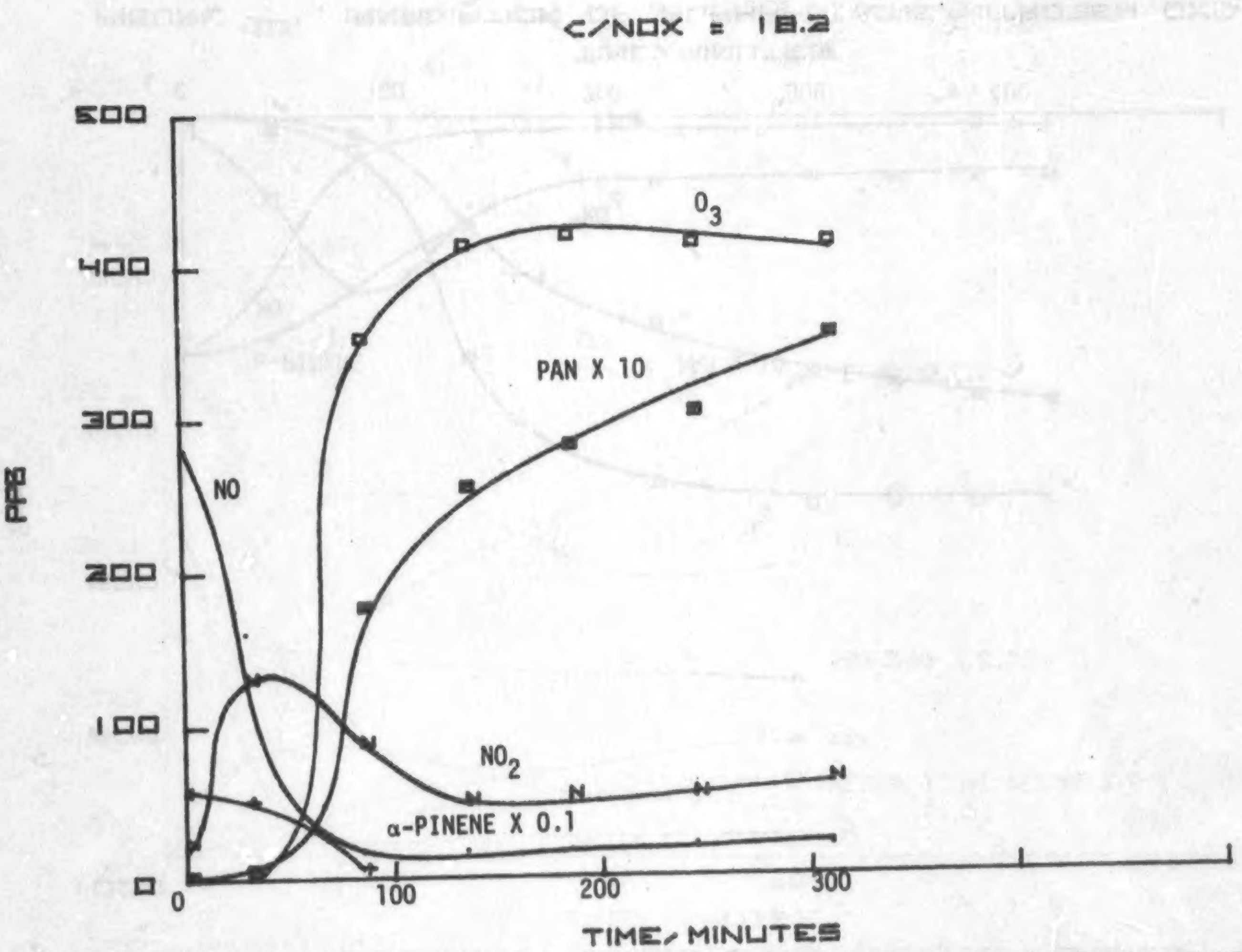


FIGURE 22B. IRRADIATION OF ALPHA-PINENE/NITROGEN OXIDES

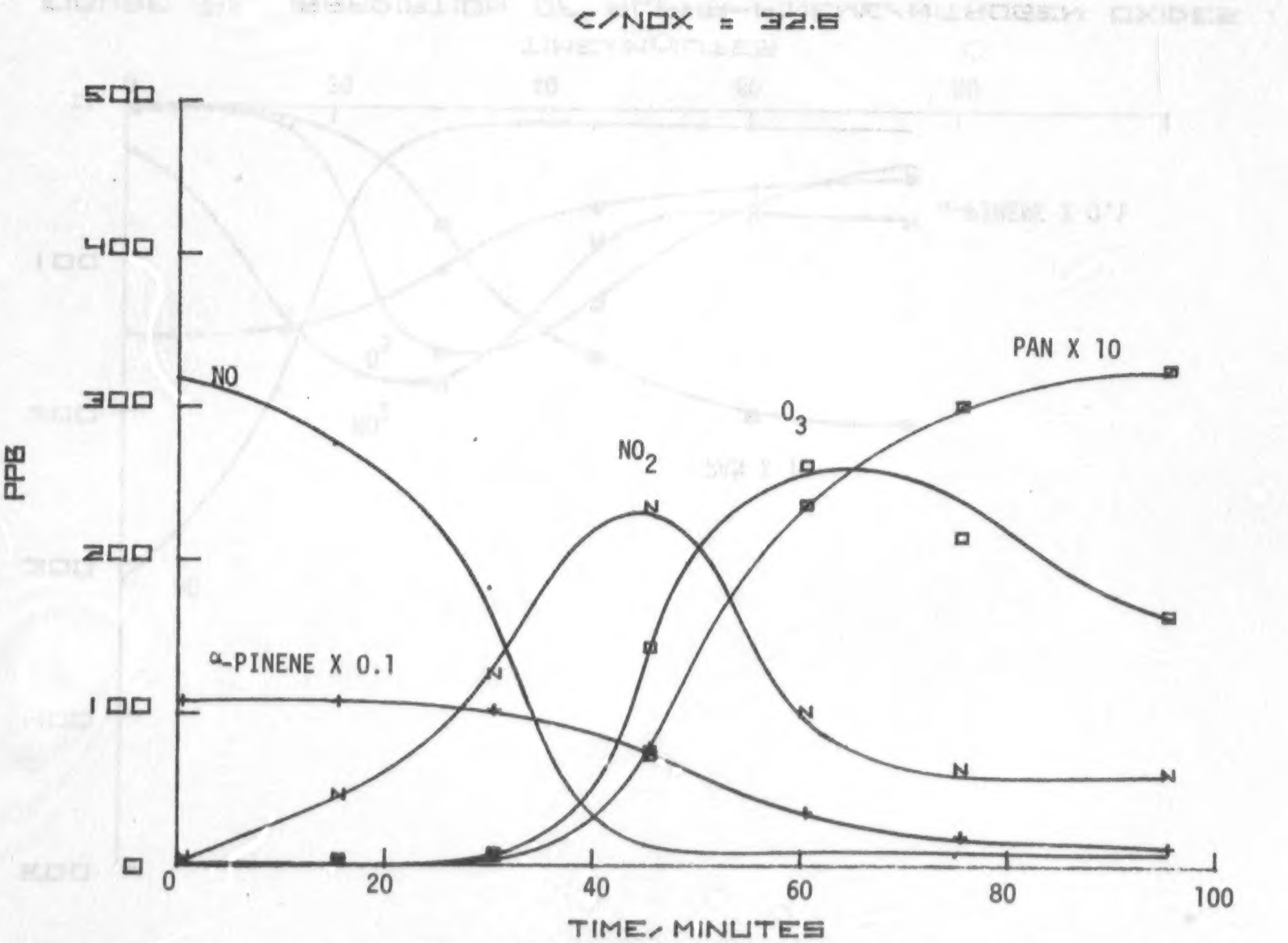


FIGURE 23B. IRRADIATION OF ALPHA-PINENE/NITROGEN OXIDES

C/NOX = 43.3

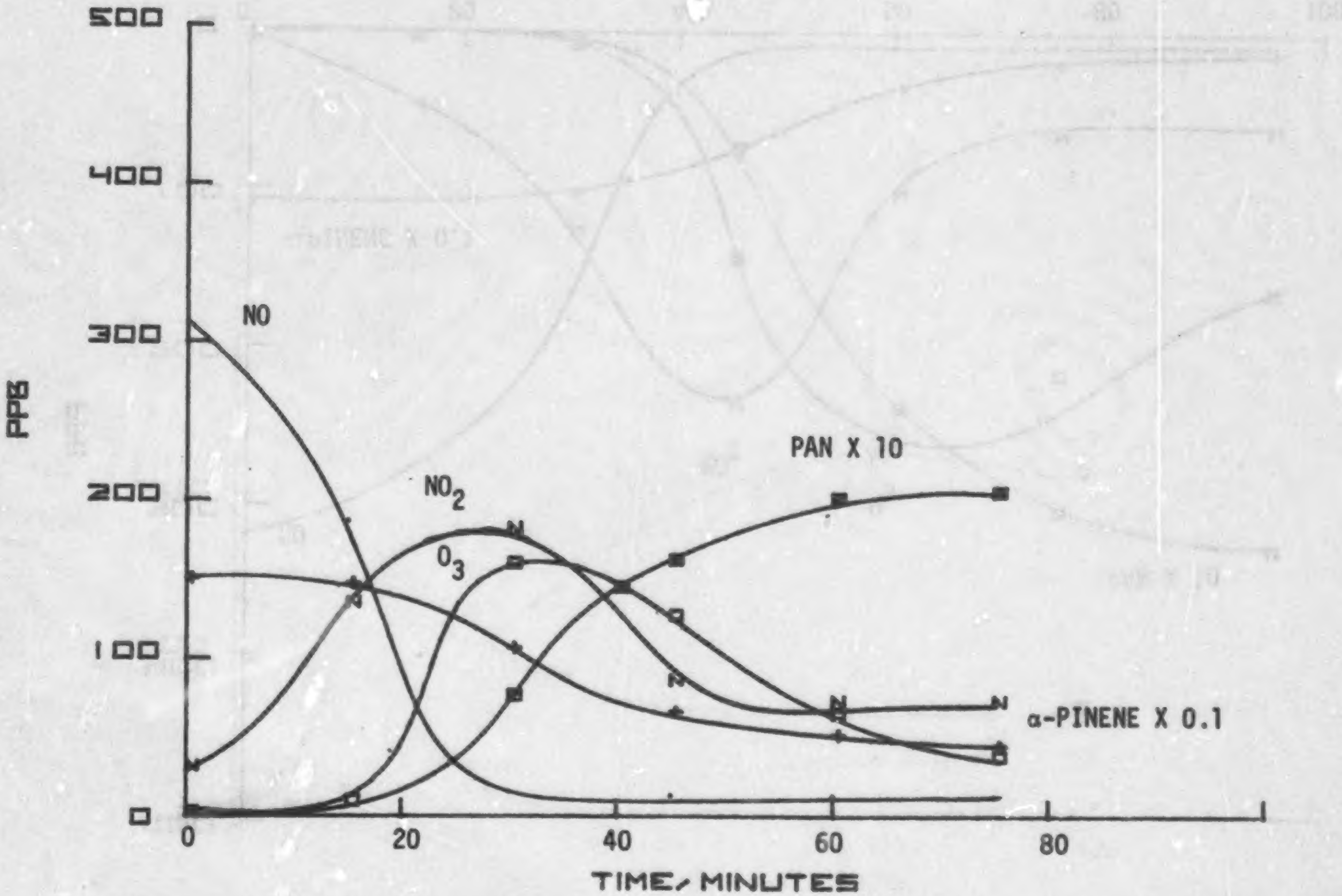


FIGURE 24B. IRRADIATION OF ALPHA-PINENE/NITROGEN OXIDES

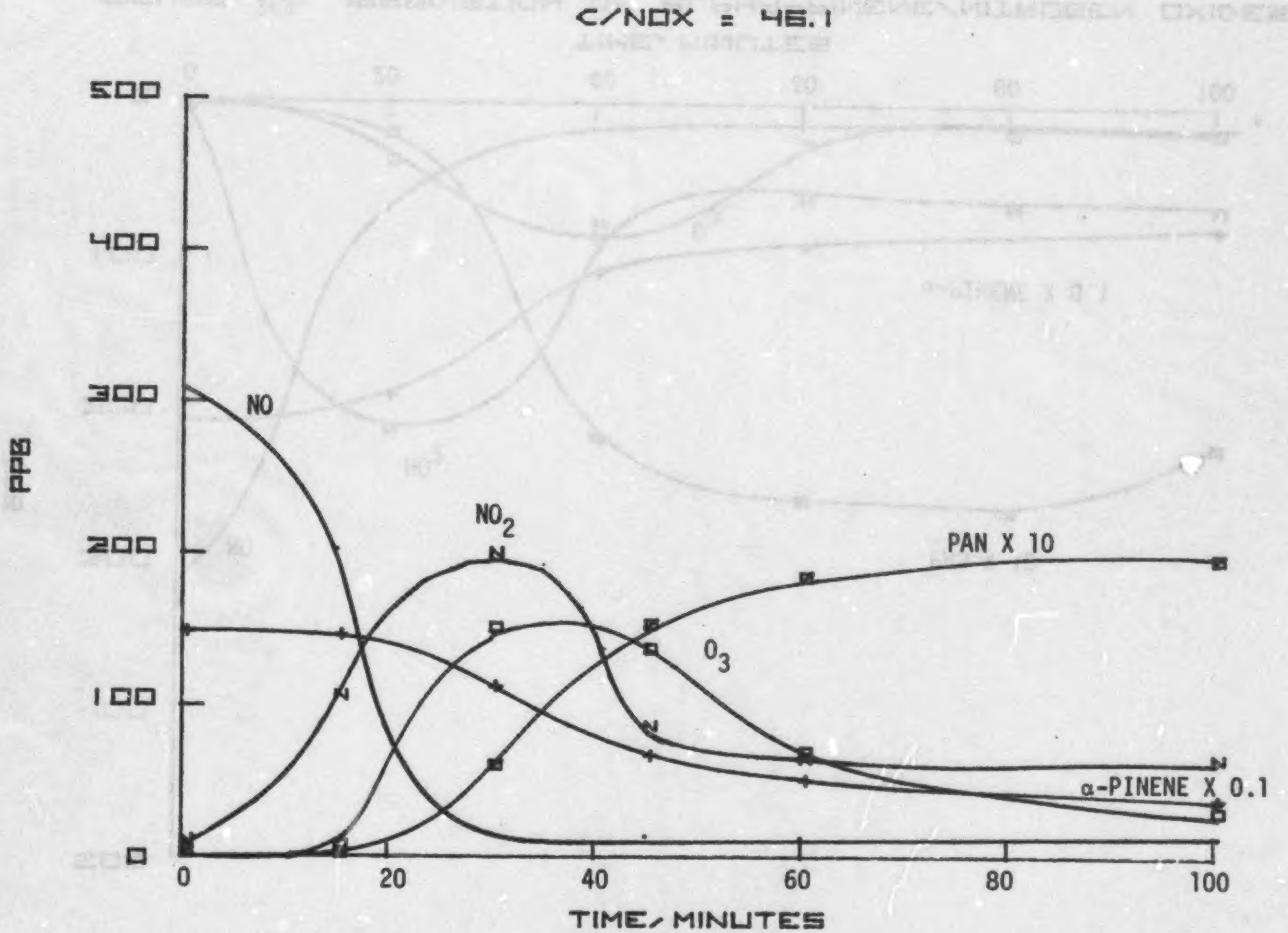


FIGURE 25B. IRRADIATION OF ALPHA-PINENE/NITROGEN OXIDES

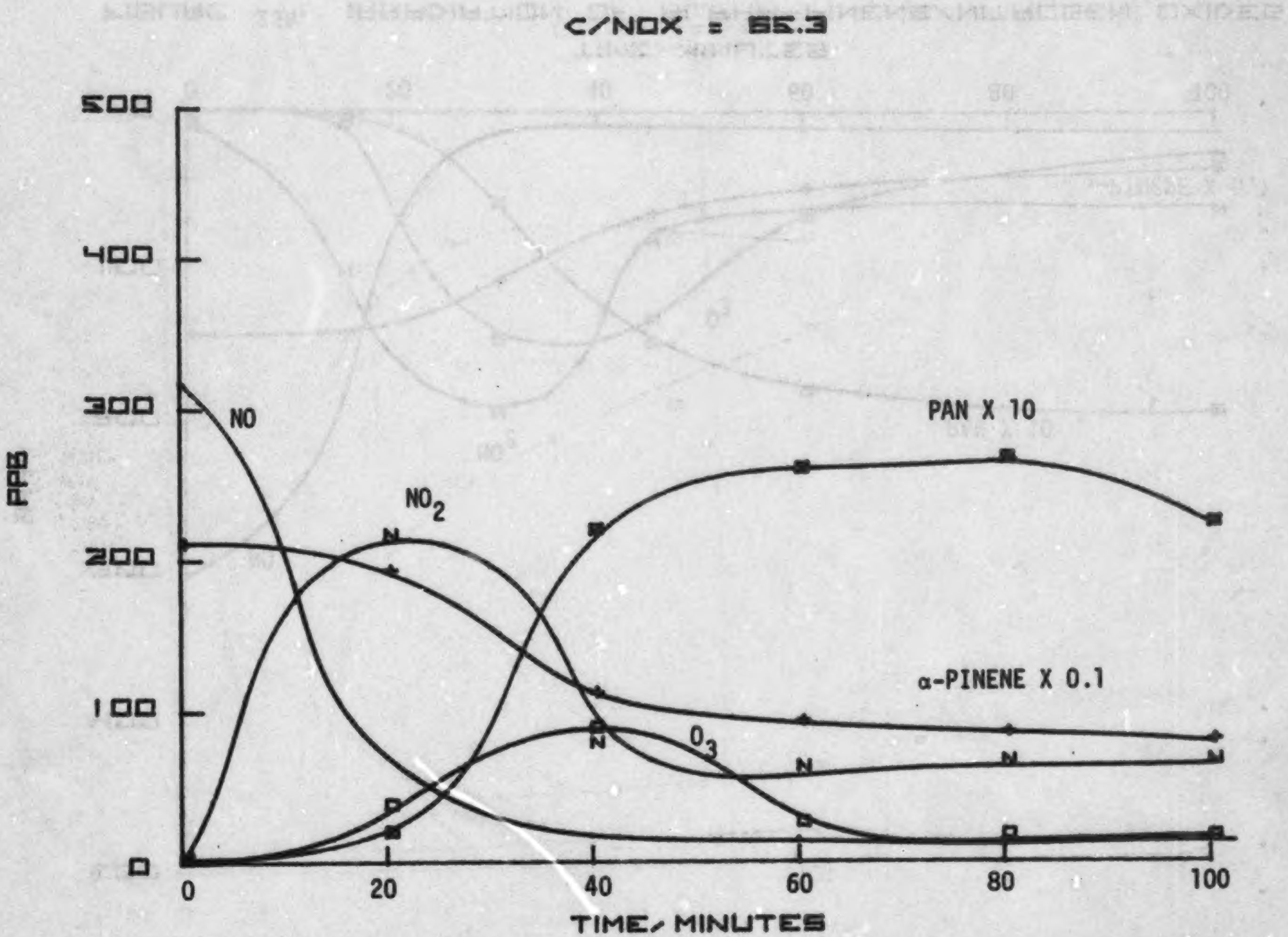


FIGURE 26B. IRRADIATION OF ALPHA-PINENE/NITROGEN OXIDES

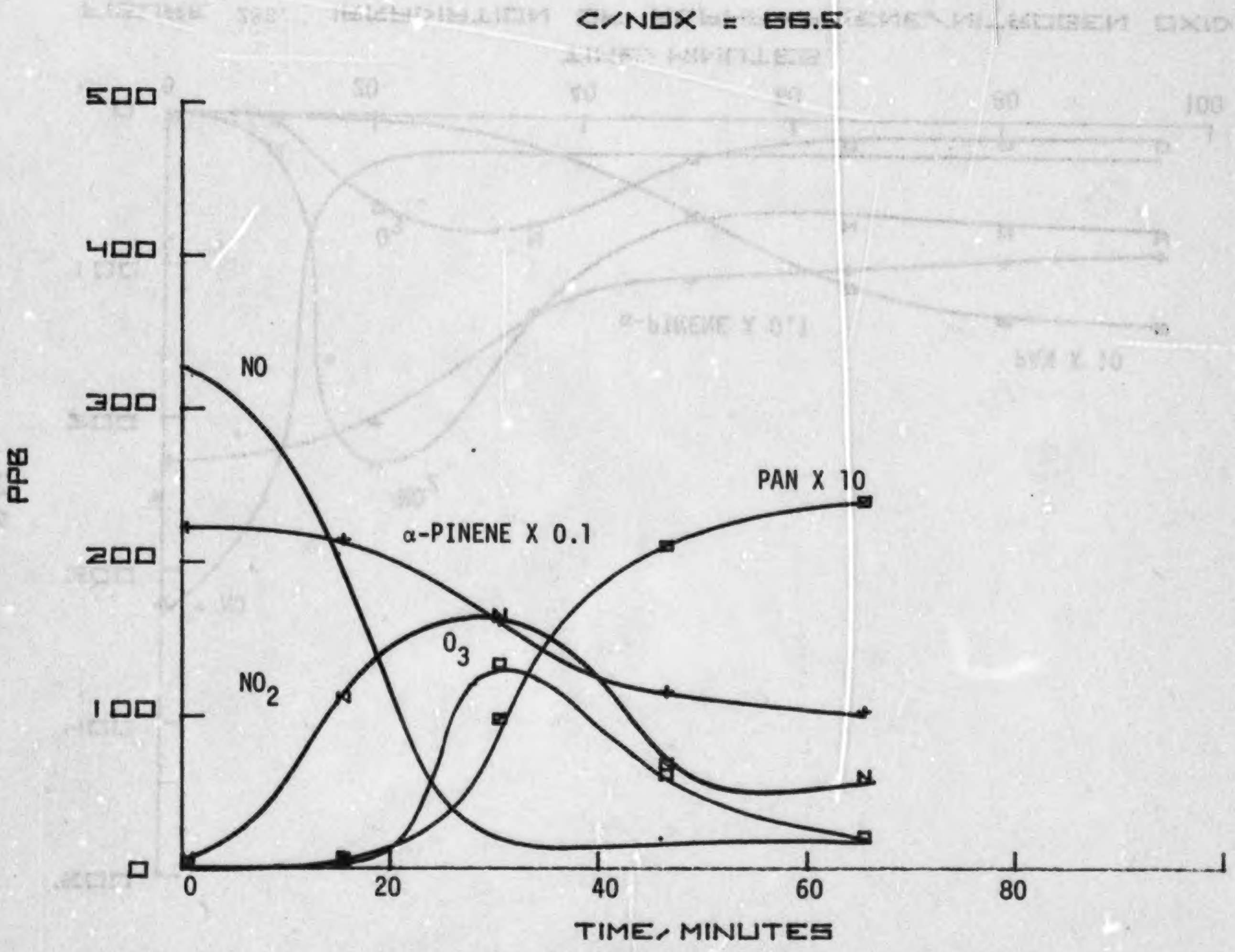


FIGURE 27B. IRRADIATION OF ALPHA-PINENE/NITROGEN OXIDES

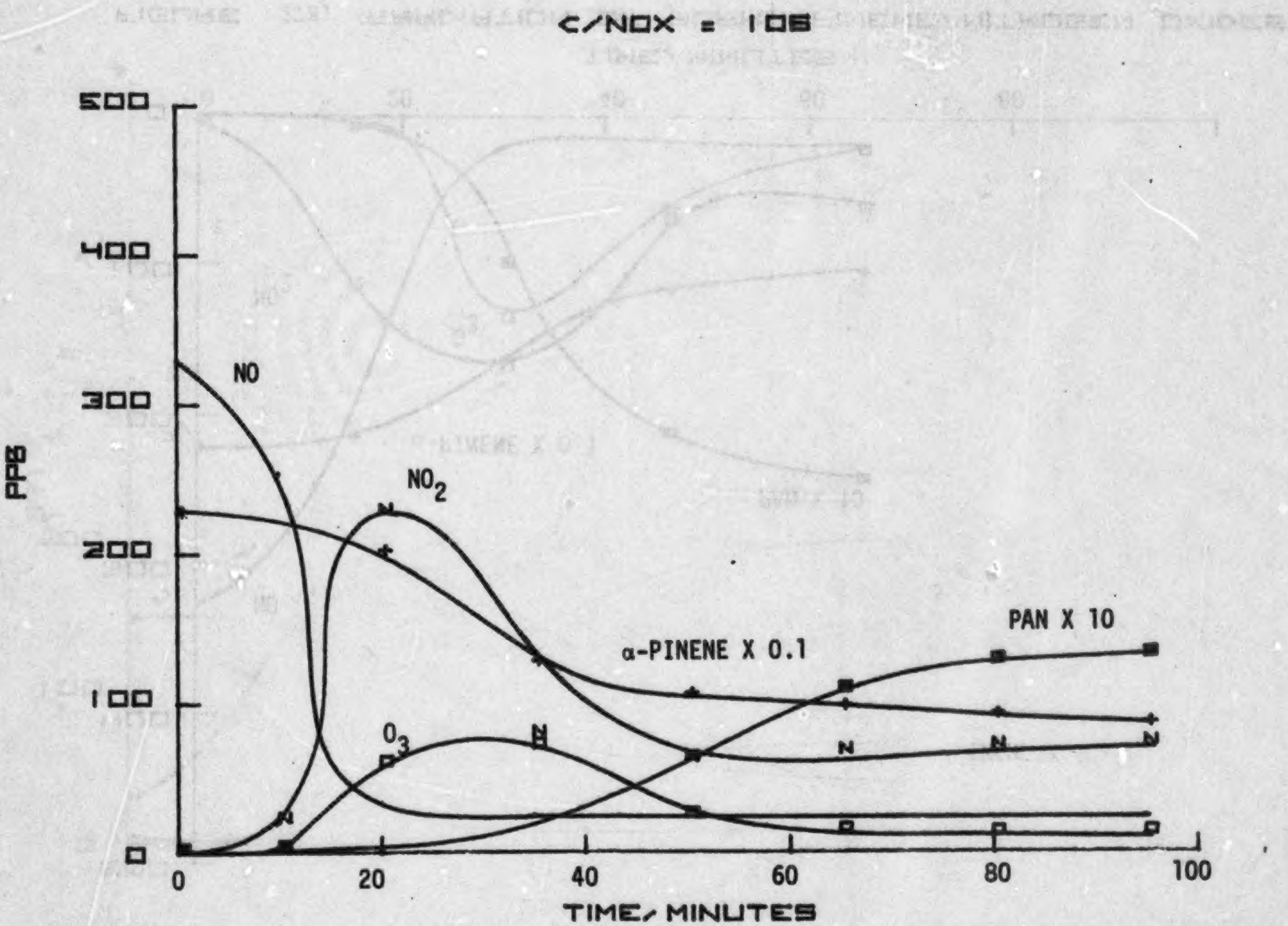


FIGURE 28B. IRRADIATION OF ALPHA-PINENE/NITROGEN OXIDES

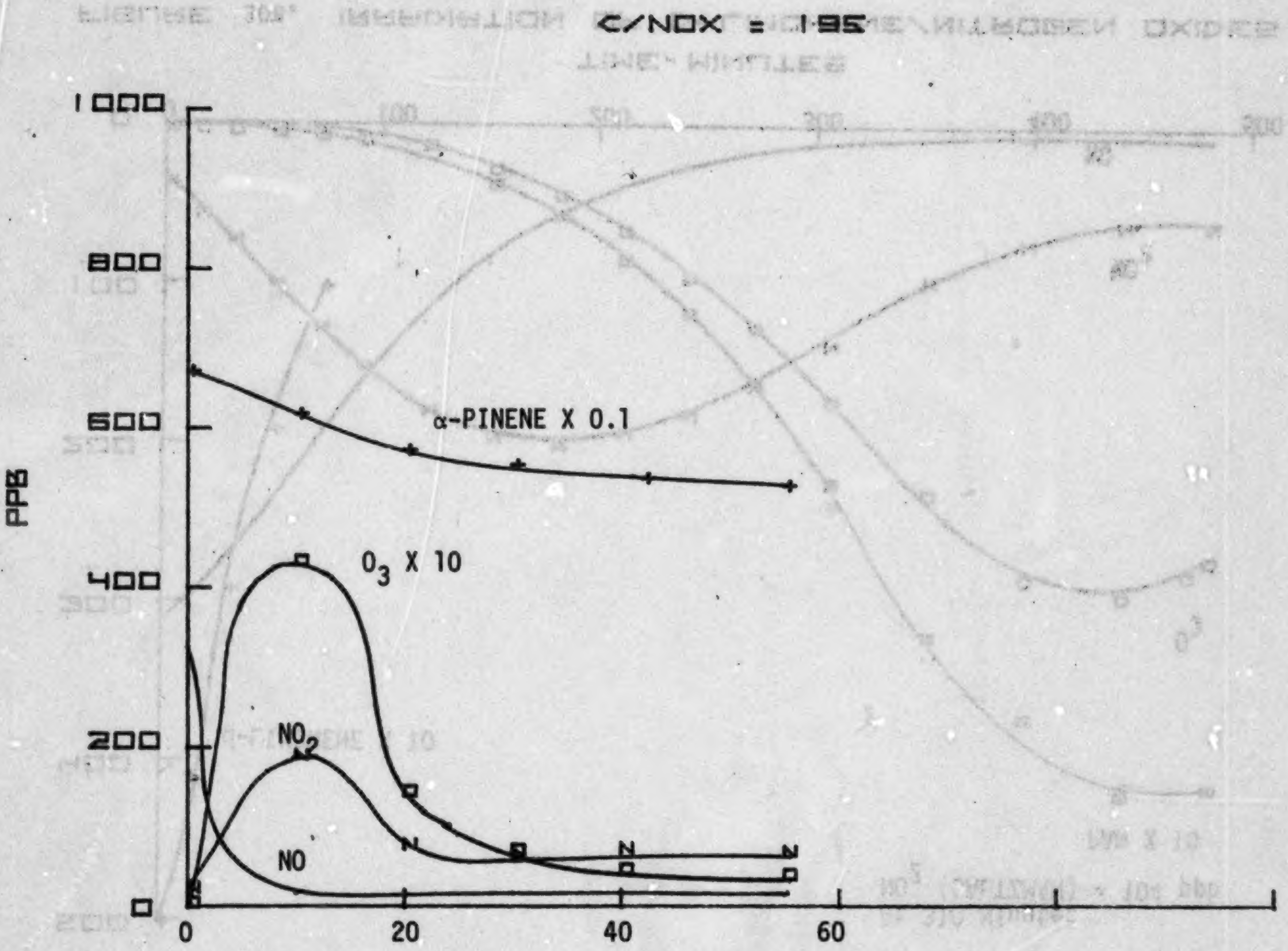


FIGURE 29B. IRRADIATION OF ALPHA-PINENE/NITROGEN OXIDES

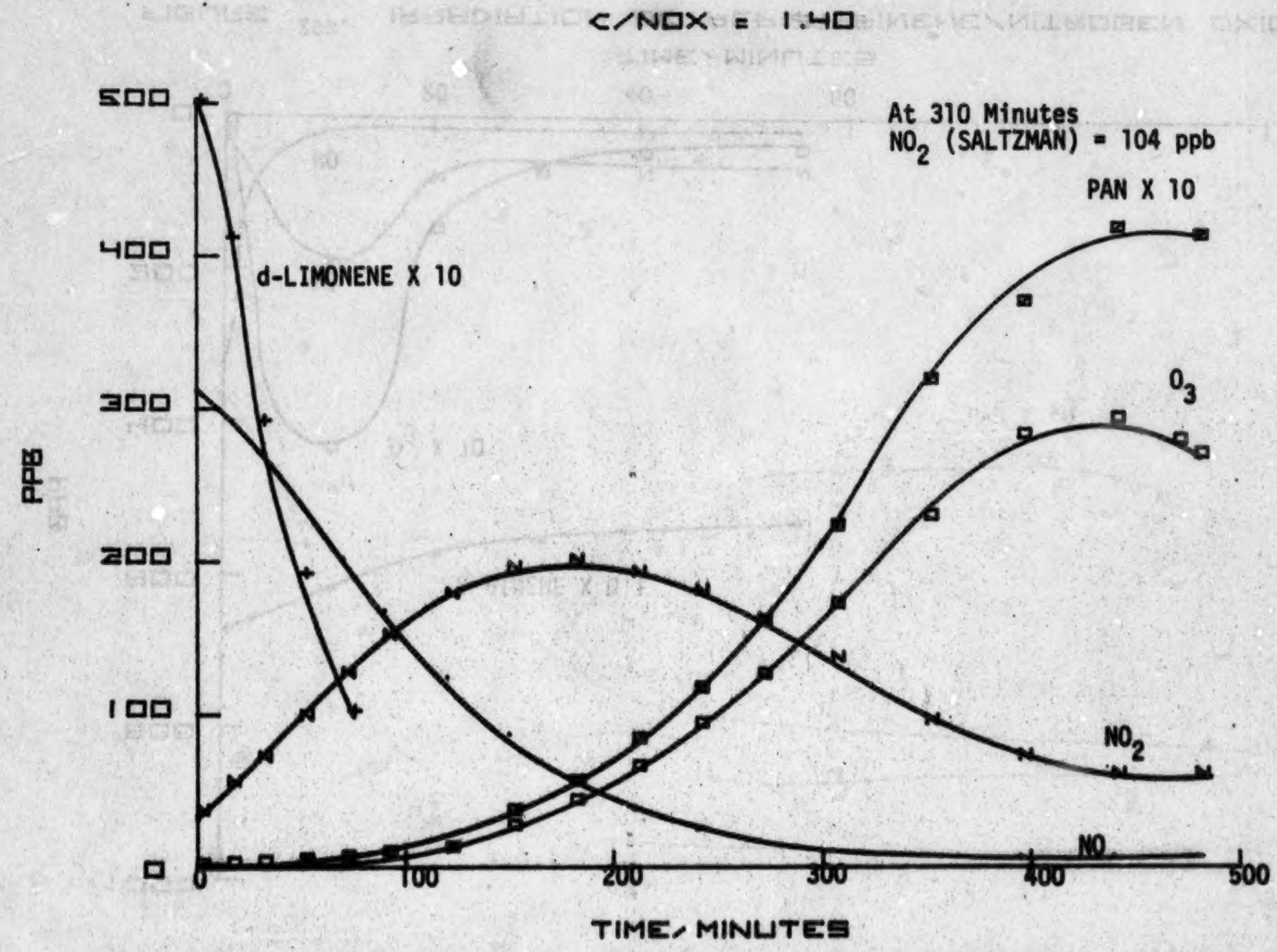


FIGURE 30B. IRRADIATION OF D-LIMONENE/NITROGEN OXIDES

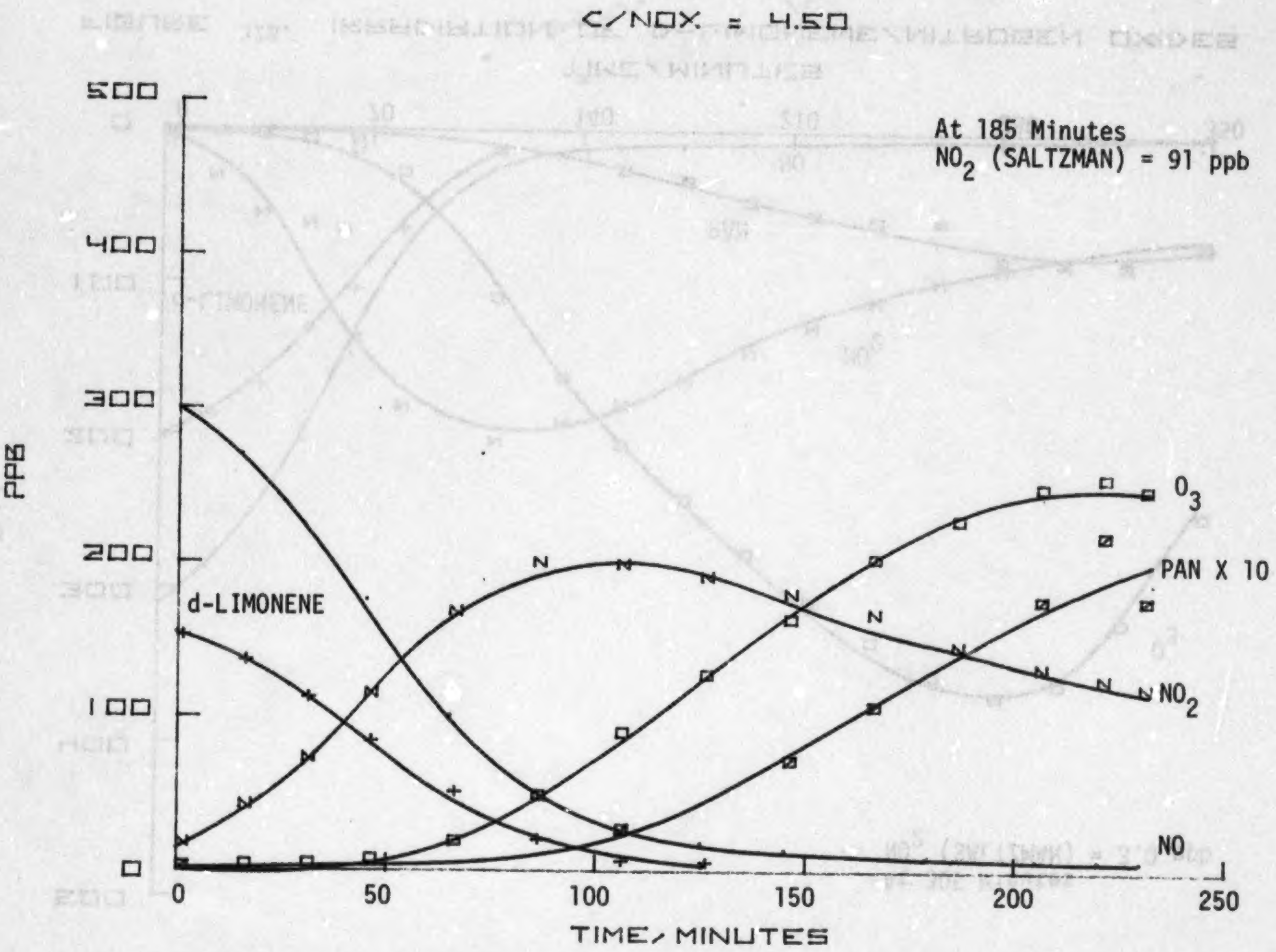


FIGURE 31B. IRRADIATION OF D-LIMONENE/NITROGEN OXIDES

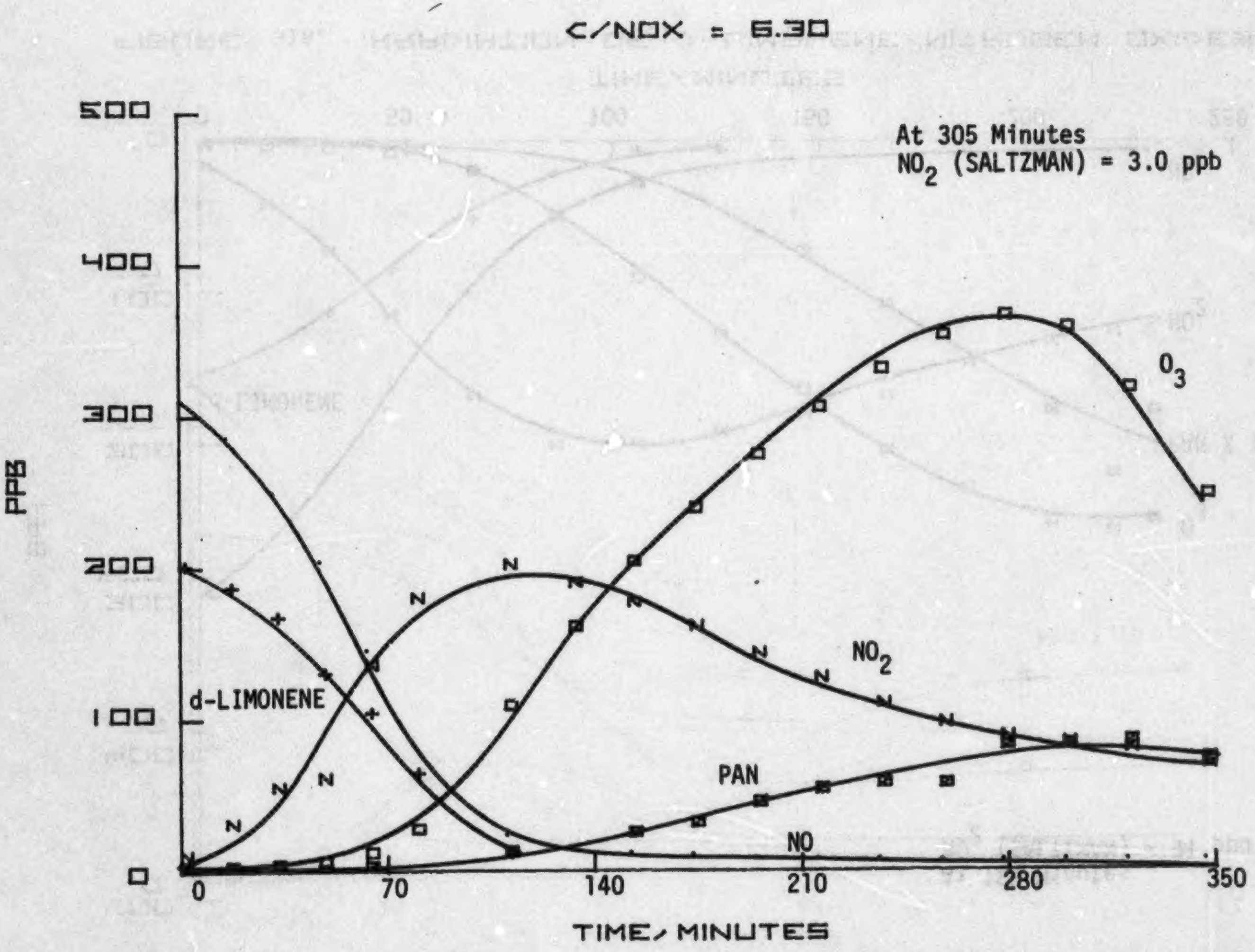


FIGURE 32B. IRRADIATION OF D-LIMONENE/NITROGEN OXIDES

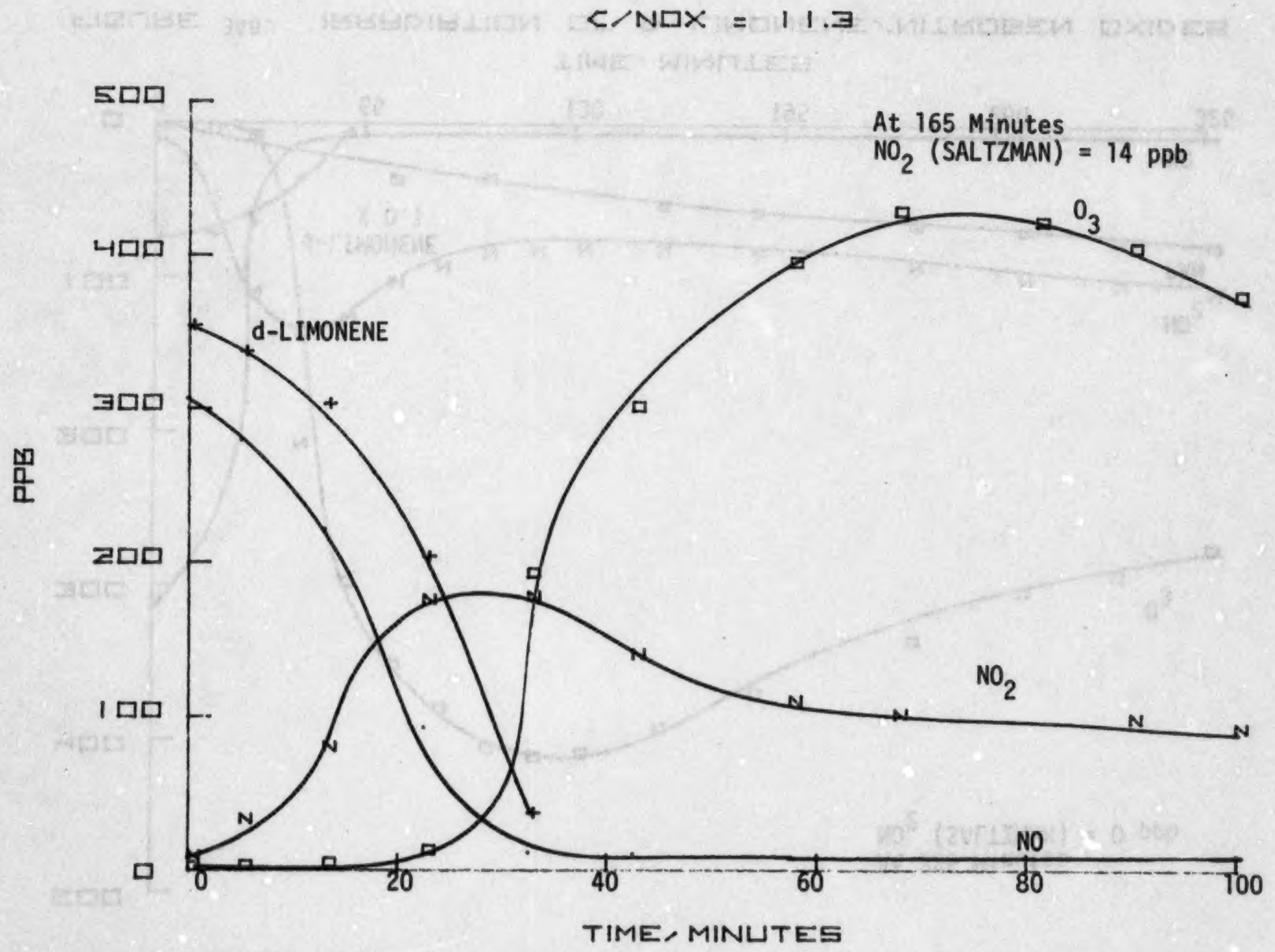


FIGURE 33B. IRRADIATION OF D-LIMONENE/NITROGEN OXIDES

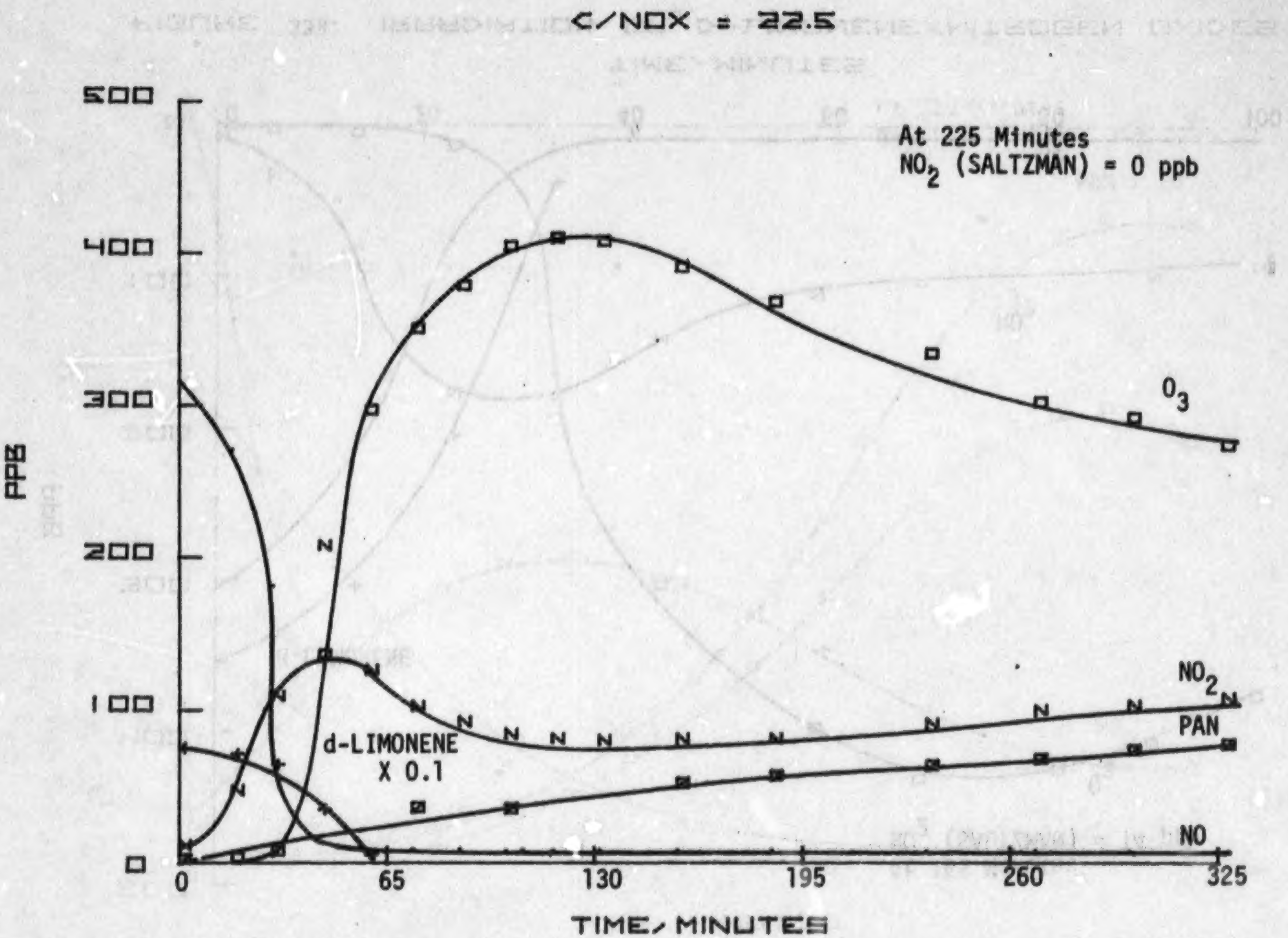


FIGURE 34B. IRRADIATION OF D-LIMONENE/NITROGEN OXIDES

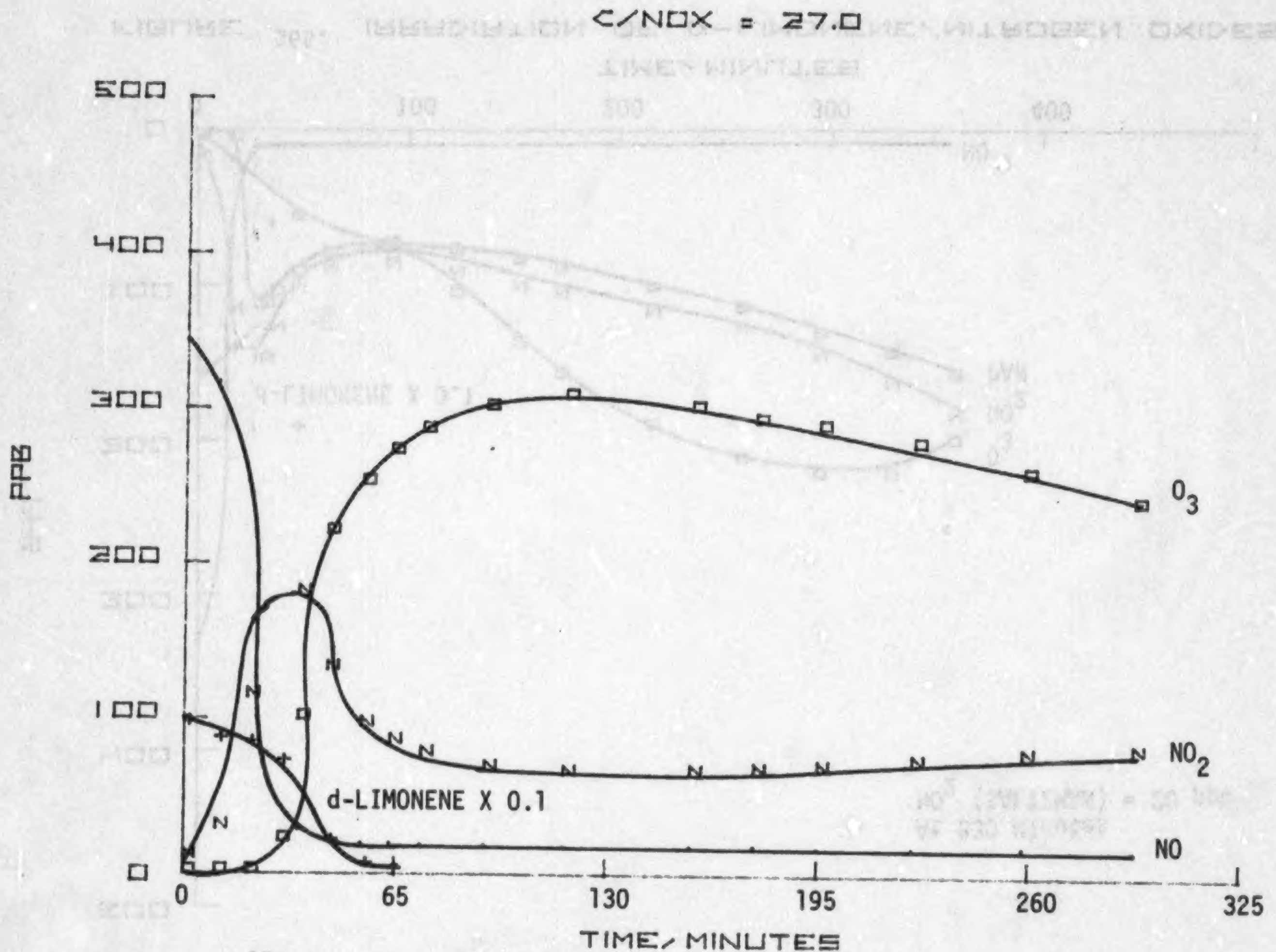


FIGURE 35B. IRRADIATION OF D-LIMONENE/NITROGEN OXIDES

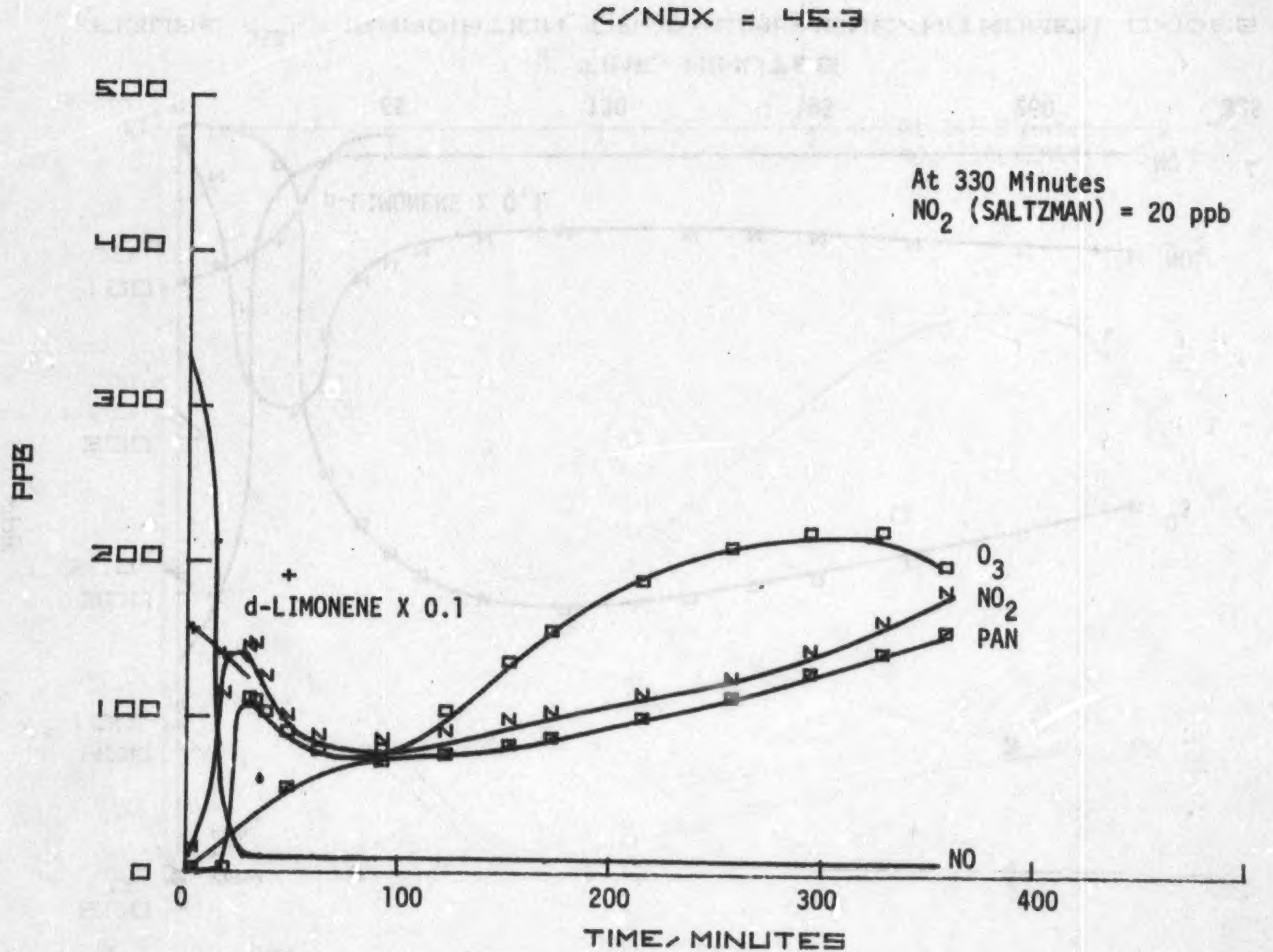


FIGURE 36B. IRRADIATION OF D-LIMONENE/NITROGEN OXIDES

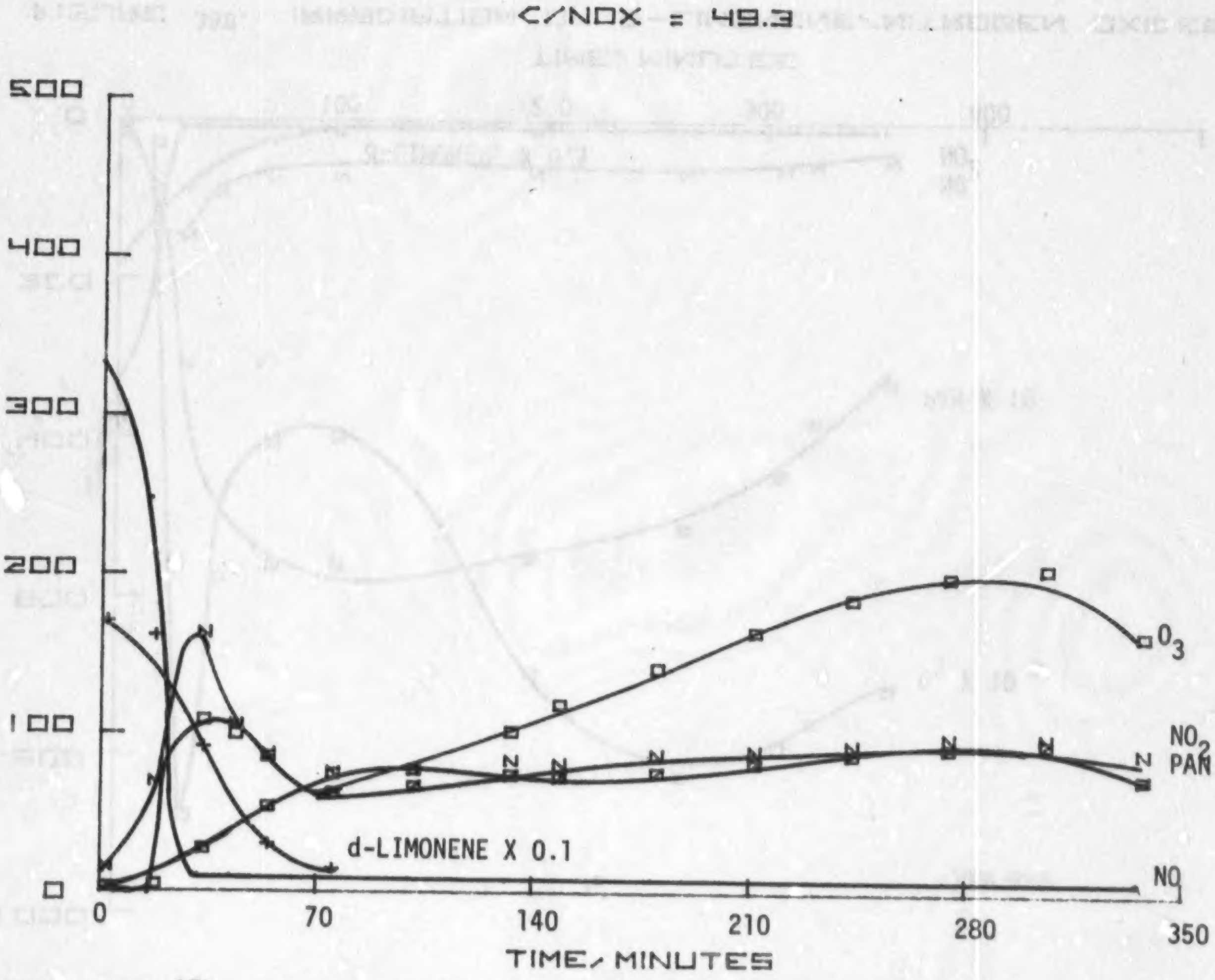


FIGURE 37B. IRRADIATION OF D-LIMONENE/NITROGEN OXIDES

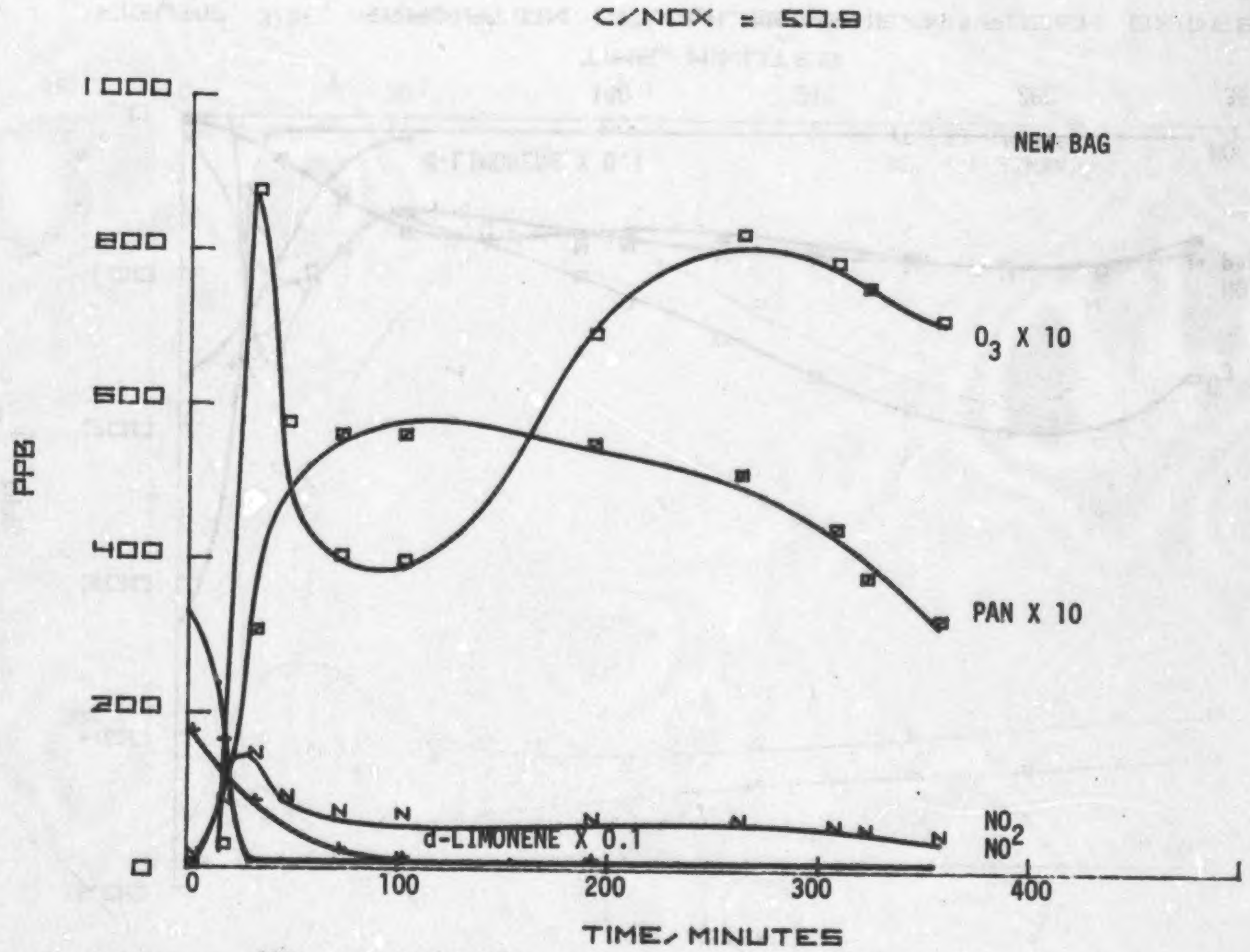


FIGURE 38B. IRRADIATION OF D-LIMONENE/NITROGEN OXIDES

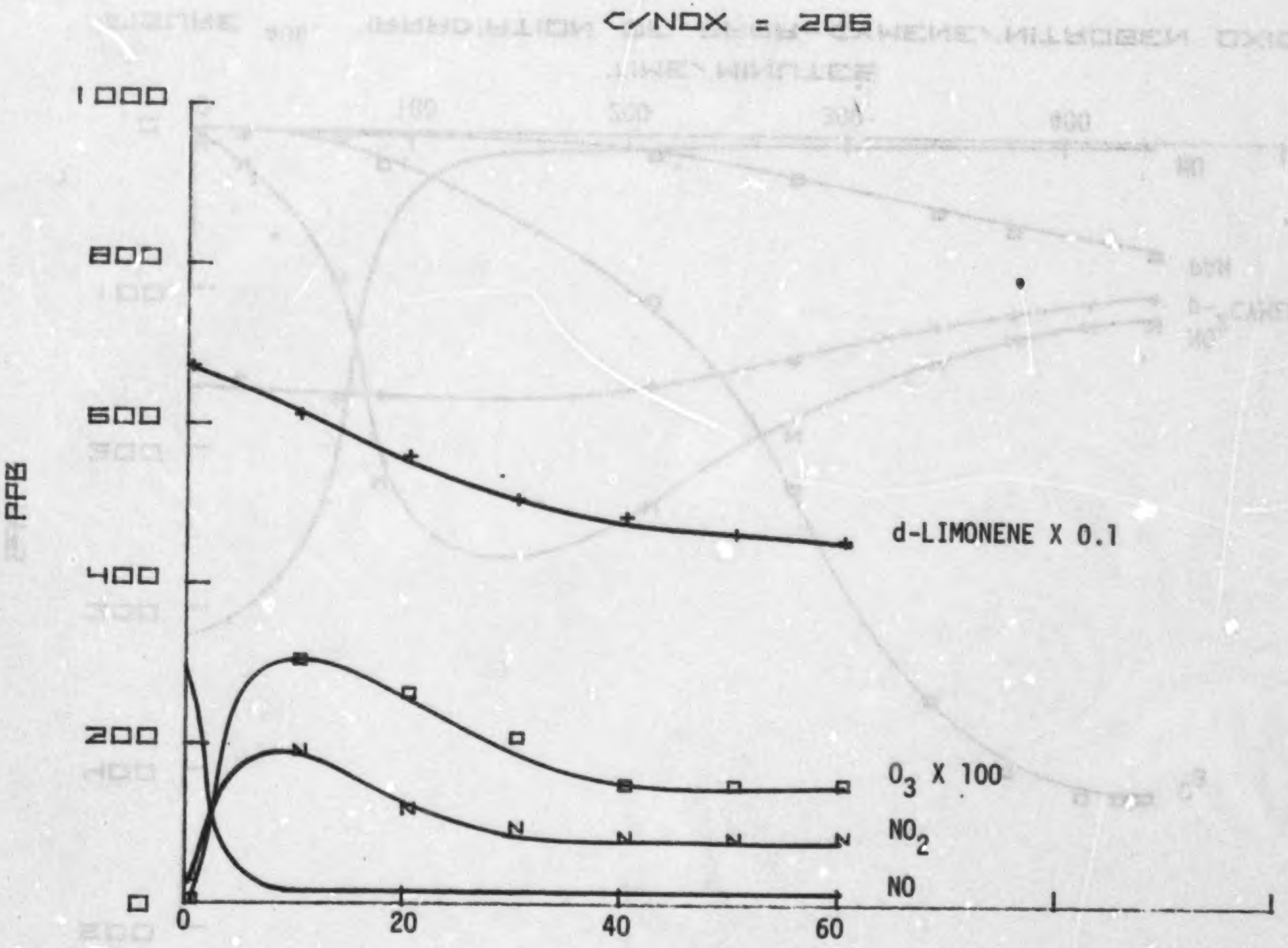


FIGURE 39B. IRRADIATION OF D-LIMONENE/NITROGEN OXIDES

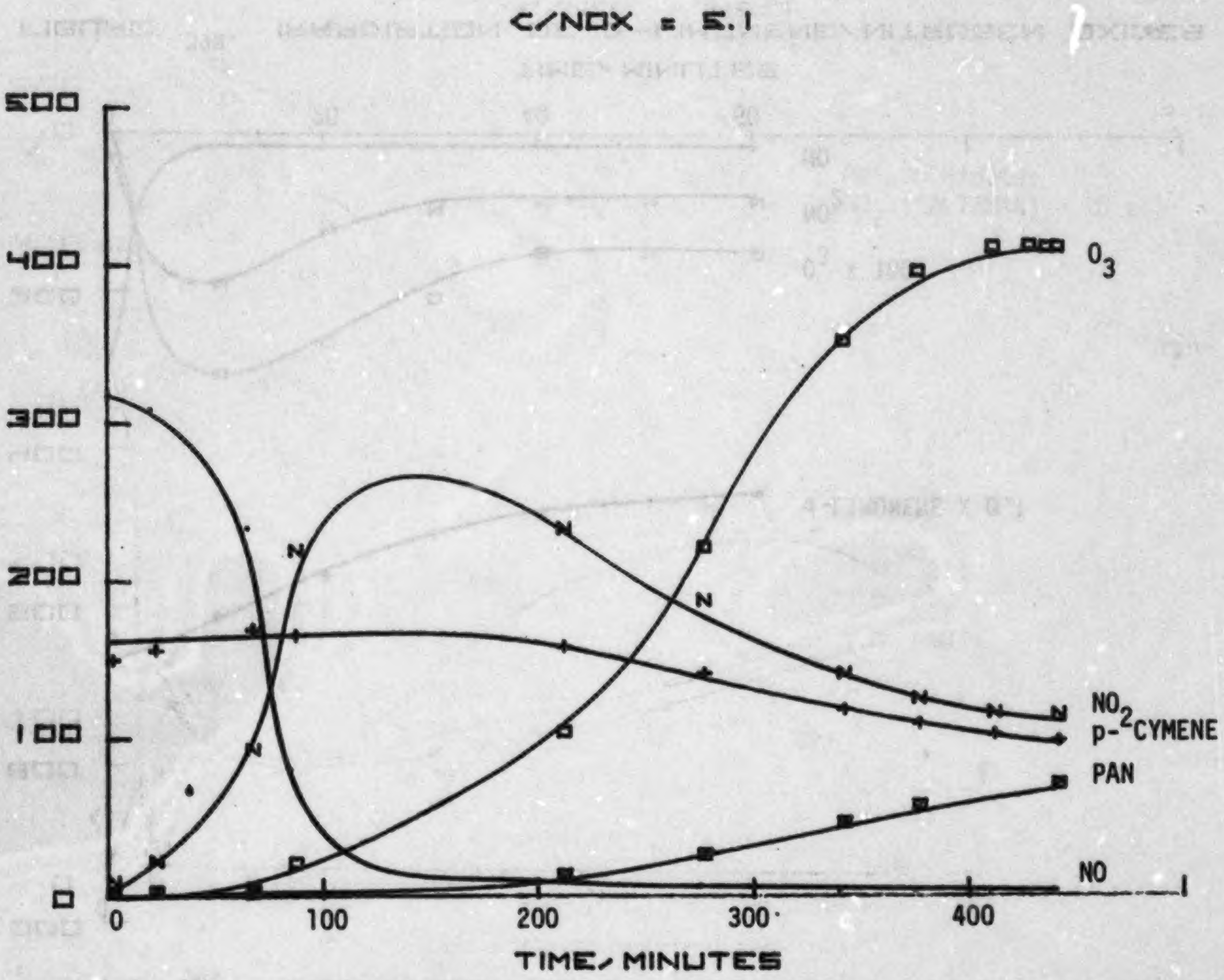


FIGURE 40B. IRRADIATION OF PARA-CYMENE/NITROGEN OXIDES

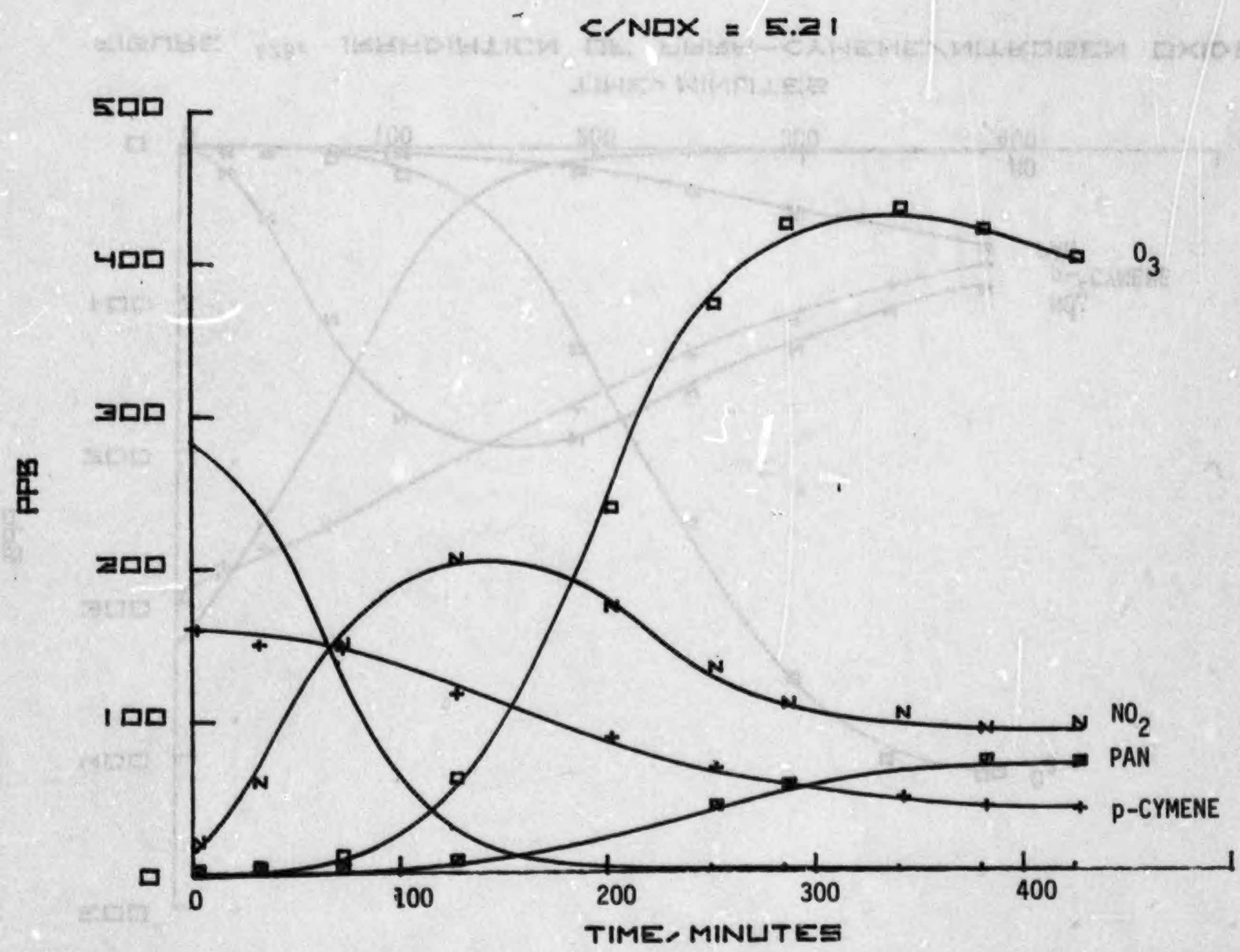


FIGURE 41. IRRADIATION OF PARA-CYMENE/NITROGEN OXIDES

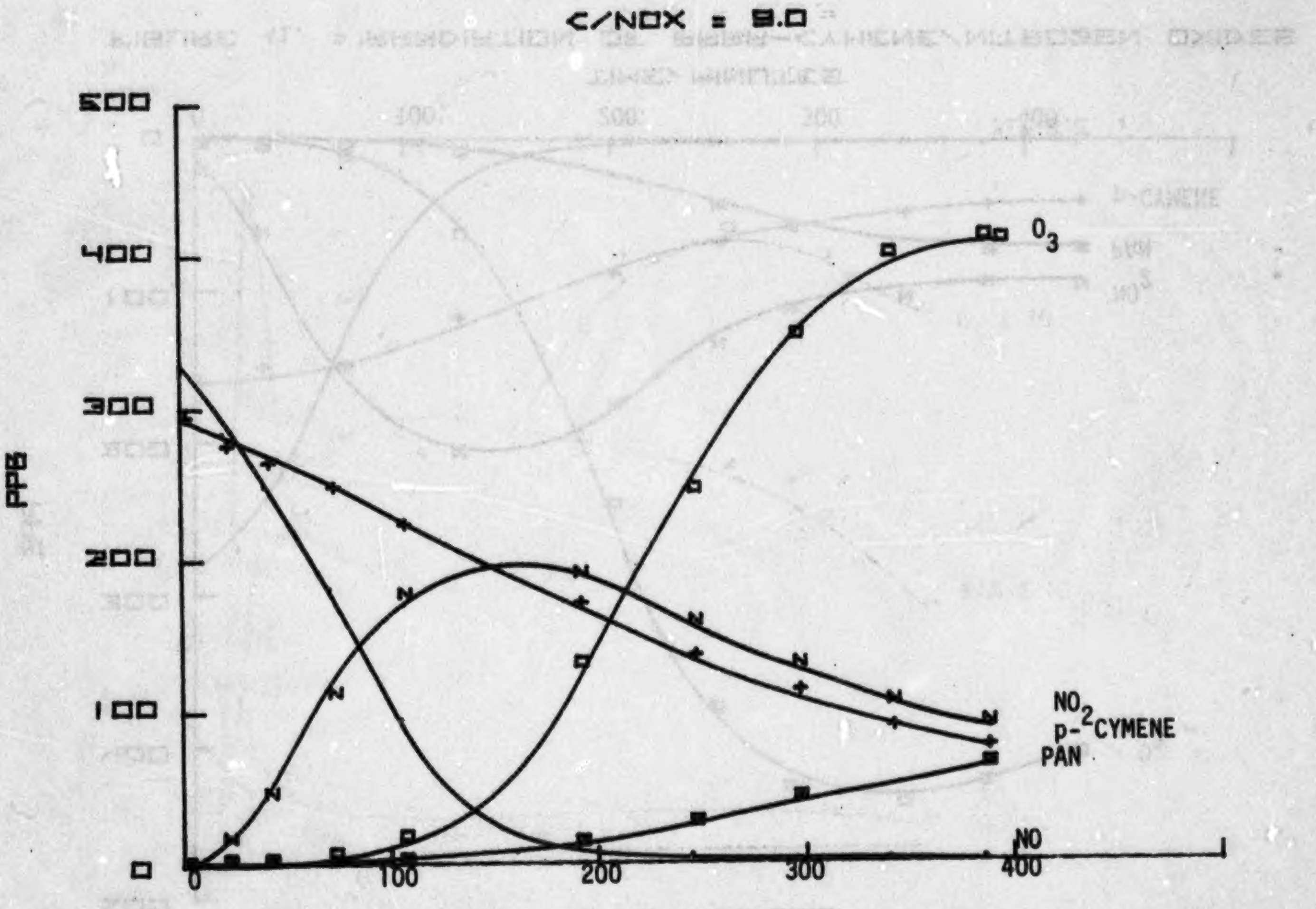


FIGURE 42B, IRRADIATION OF PARA-CYMENE/NITROGEN OXIDES

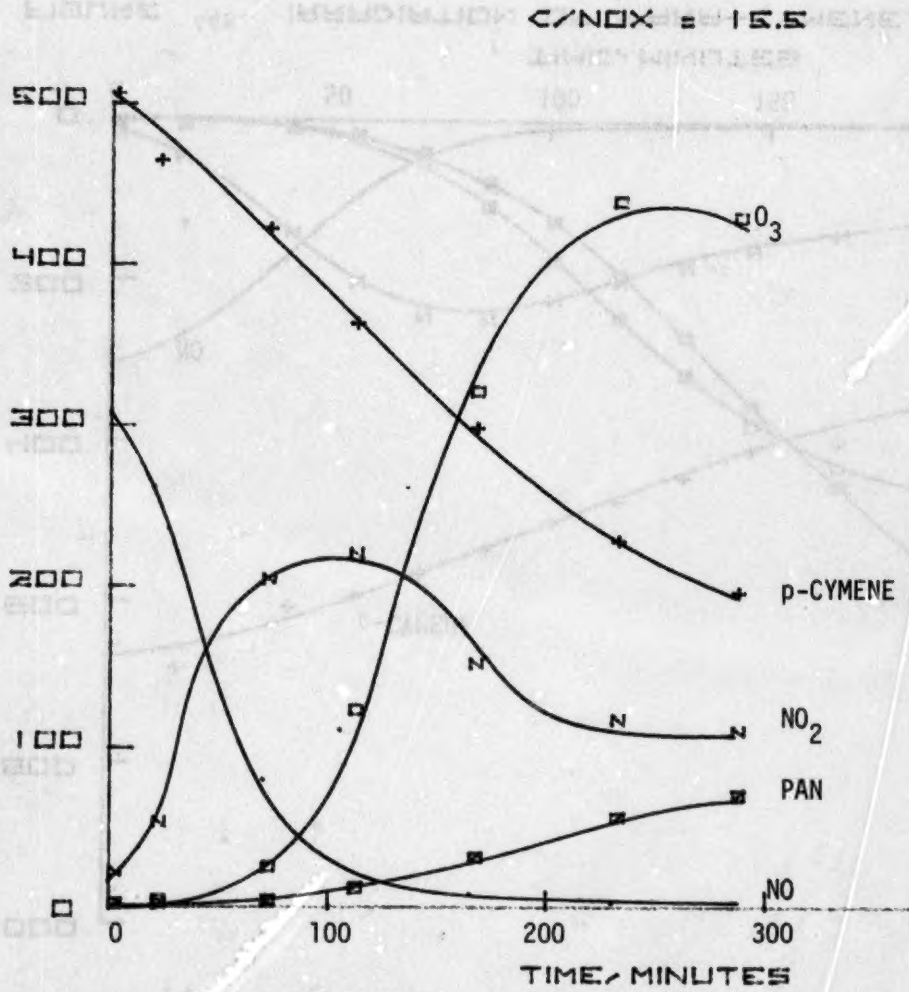


FIGURE 43B. IRRADIATION OF PARA-CYMENE/NITROGEN OXIDES

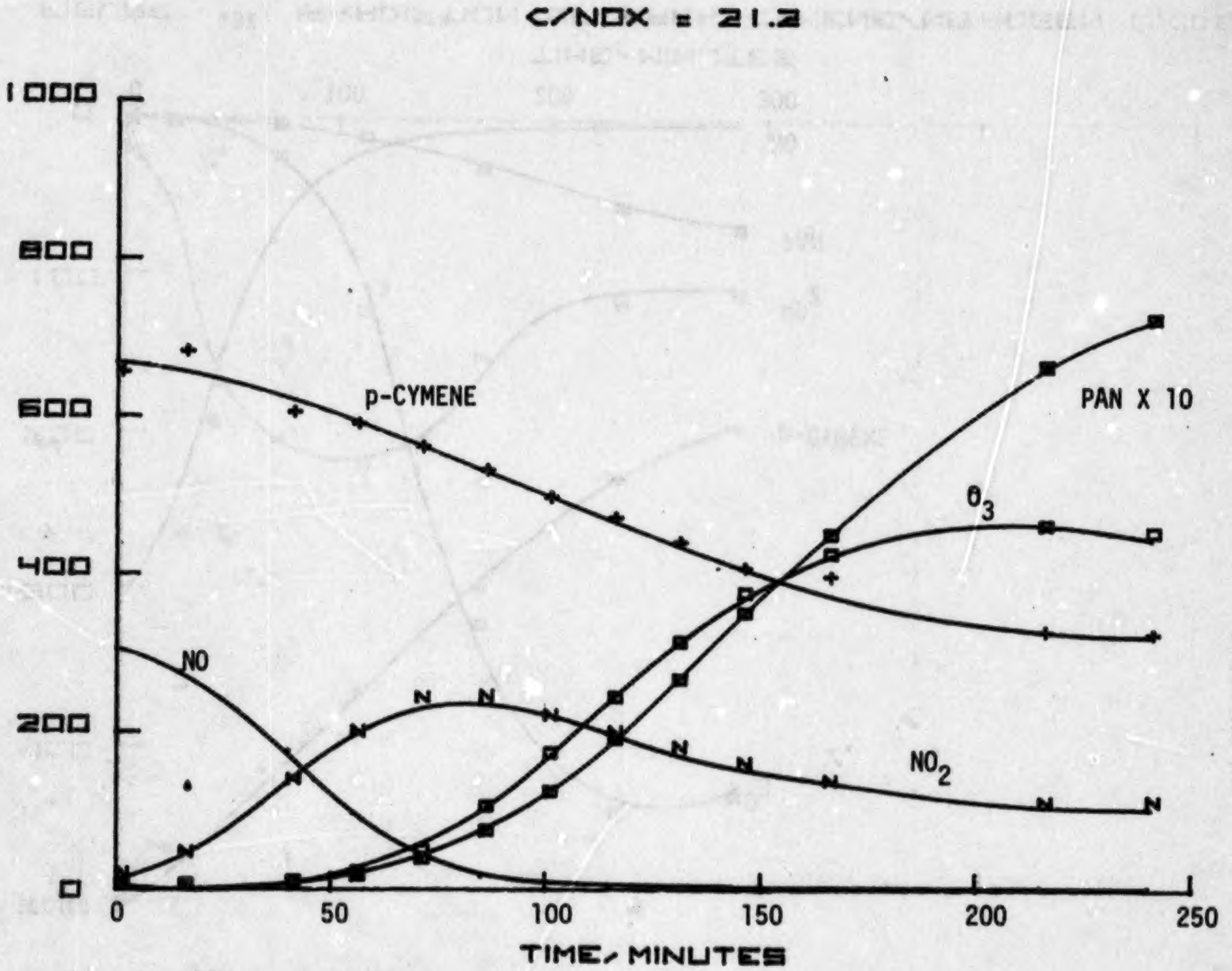


FIGURE 44B. IRRADIATION OF PARA-CYMENE/NITROGEN OXIDES

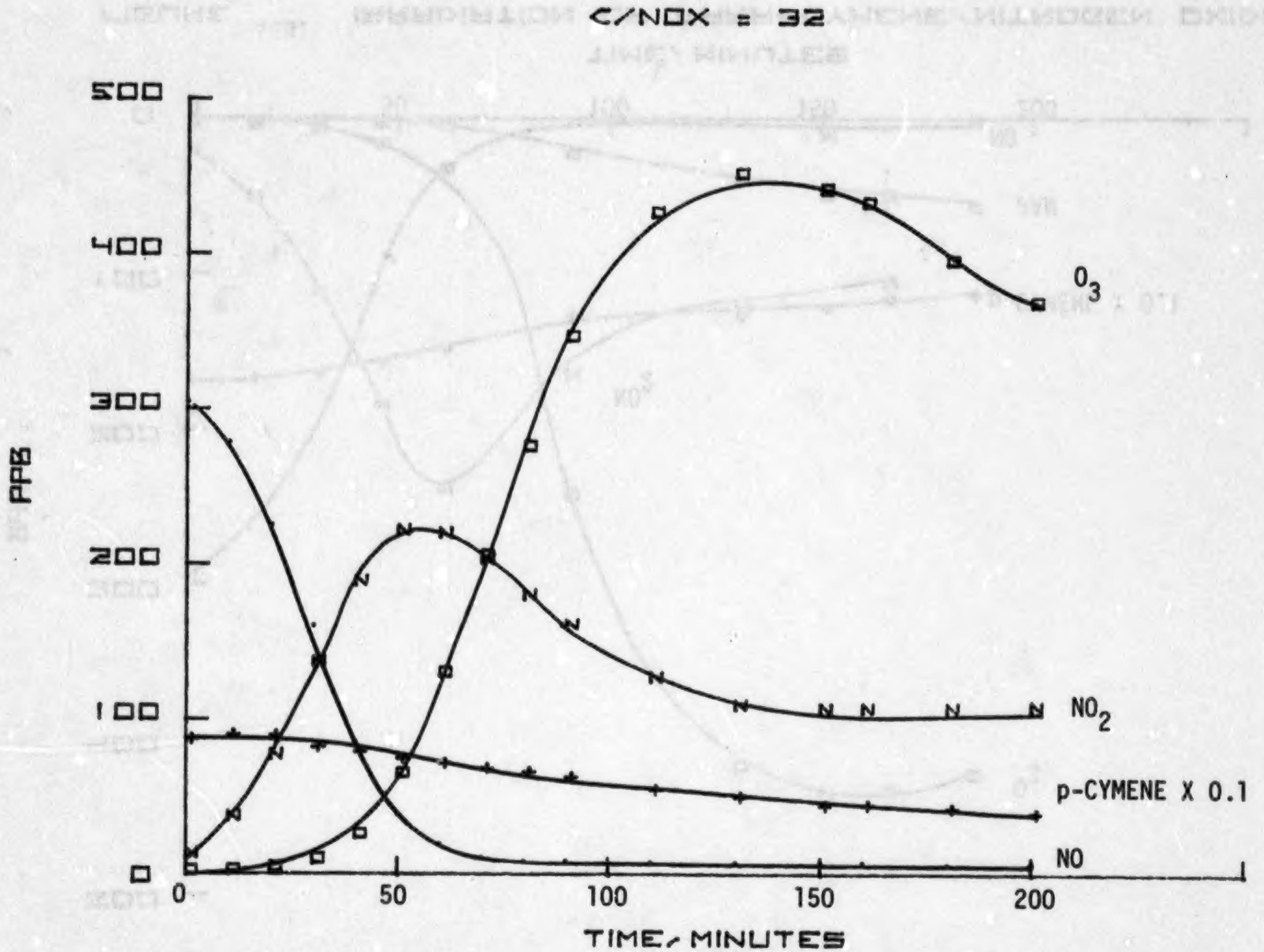


FIGURE 45B. IRRADIATION OF PARA-CYMENE/NITROGEN OXIDES

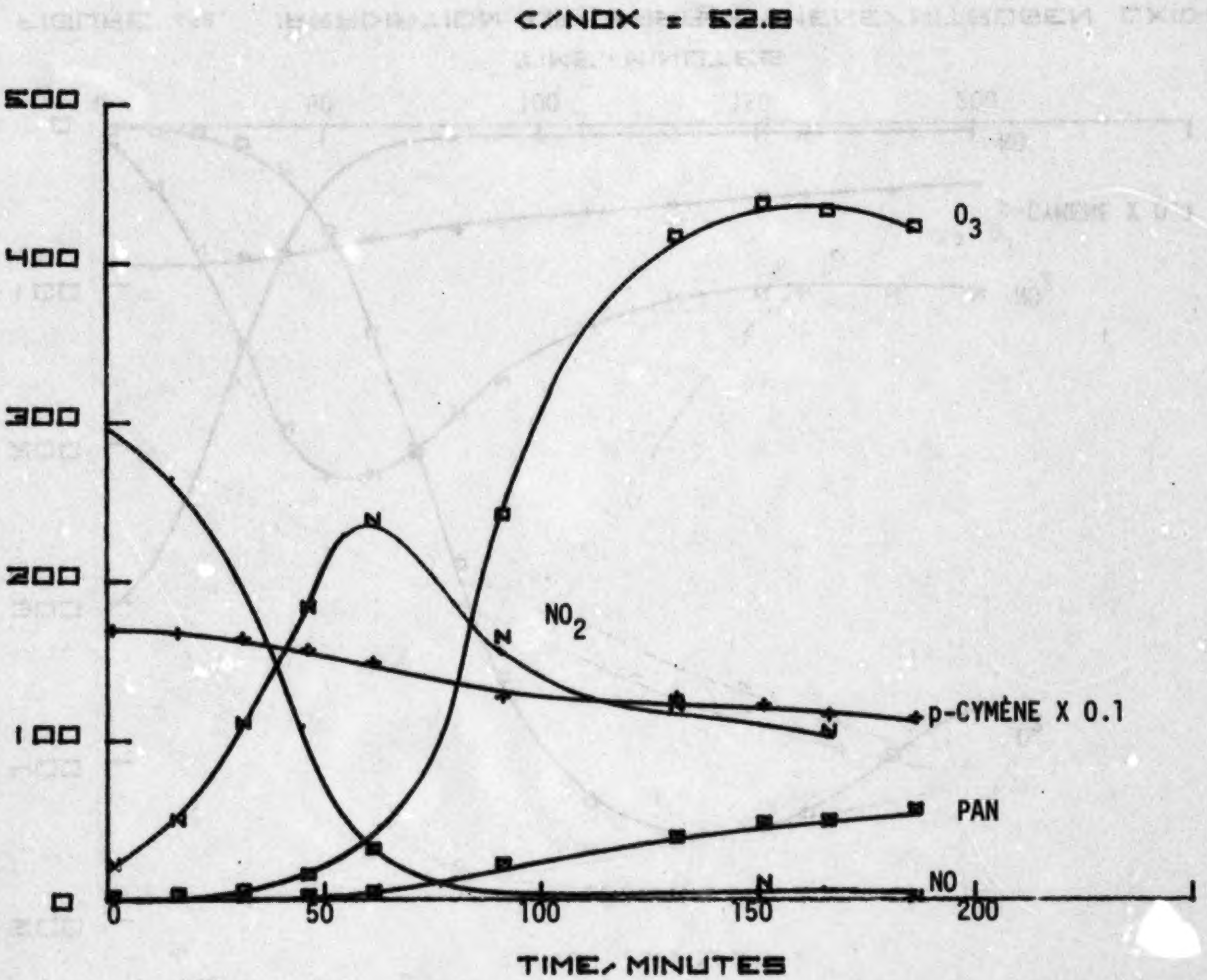


FIGURE 46B. IRRADIATION OF PARA-CYMENE/NITROGEN OXIDES

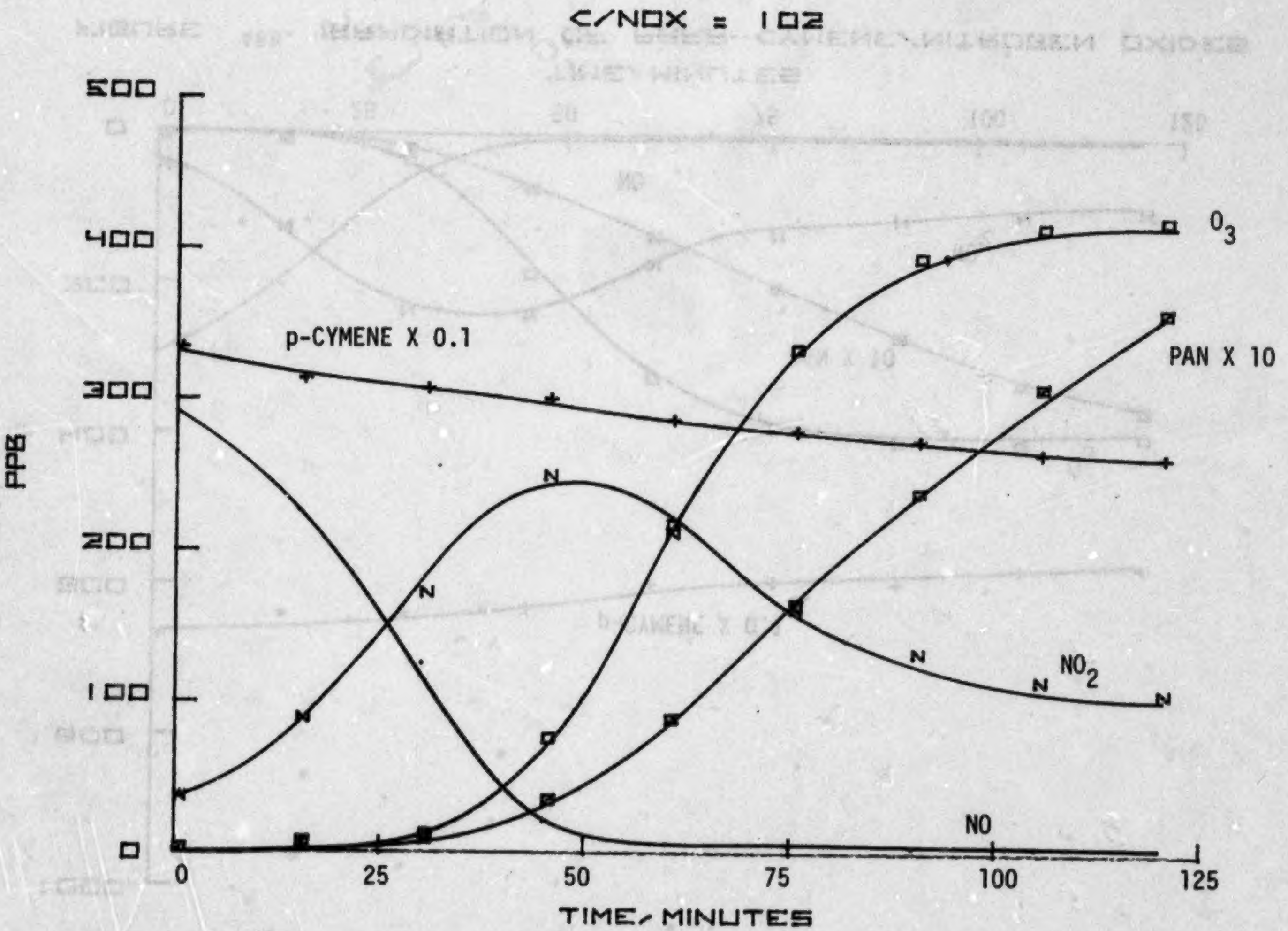


FIGURE 47B. IRRADIATION OF PARA-CYMENE/NITROGEN OXIDES

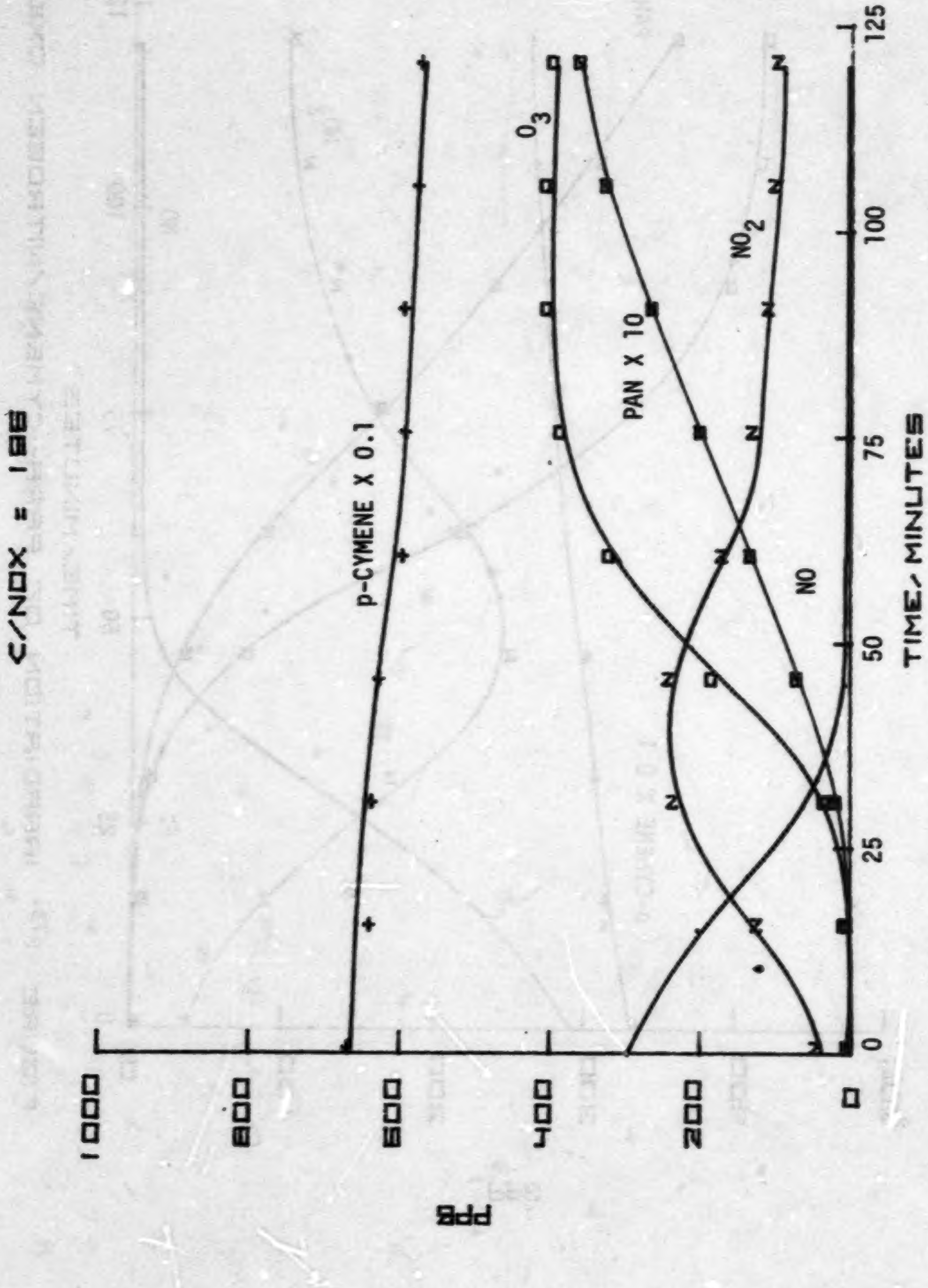


FIGURE 48B. IRRADIATION OF PARA-CYMENE/NITROGEN OXIDES

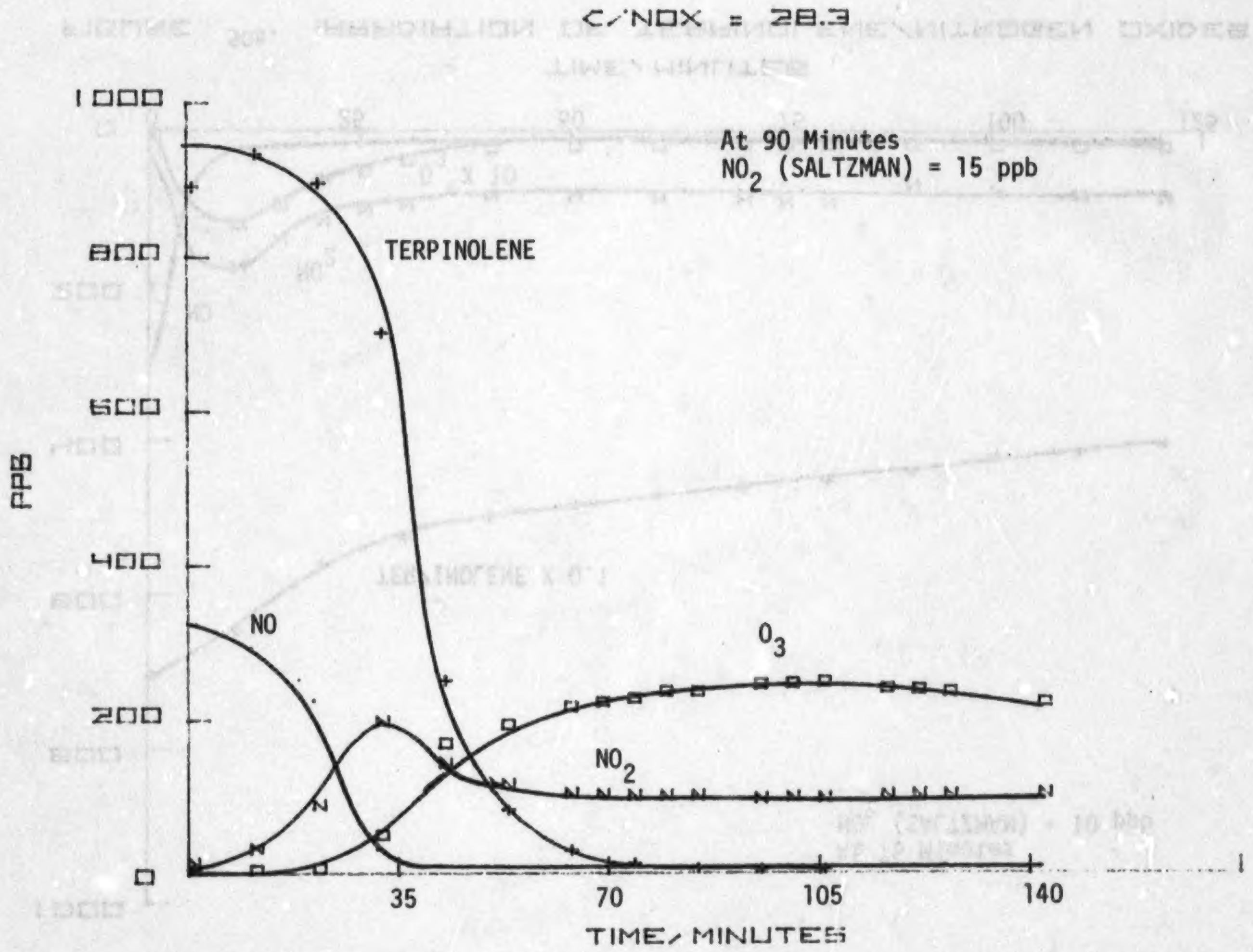


FIGURE 49B. IRRADIATION OF TERPINOLENE/NITROGEN OXIDES

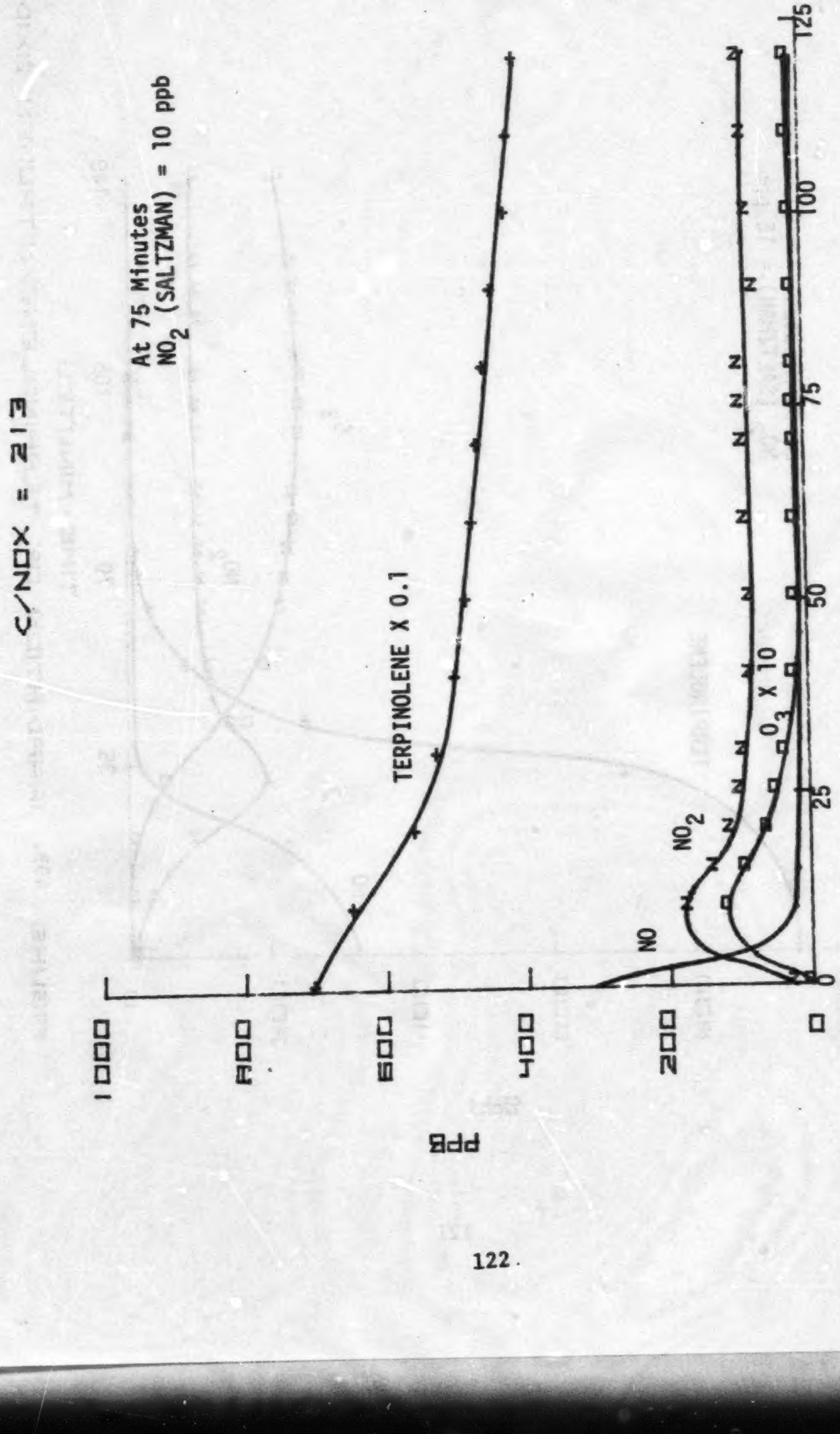


FIGURE 50B. IRRADIATION OF TERPINOLENE/NITROGEN OXIDES

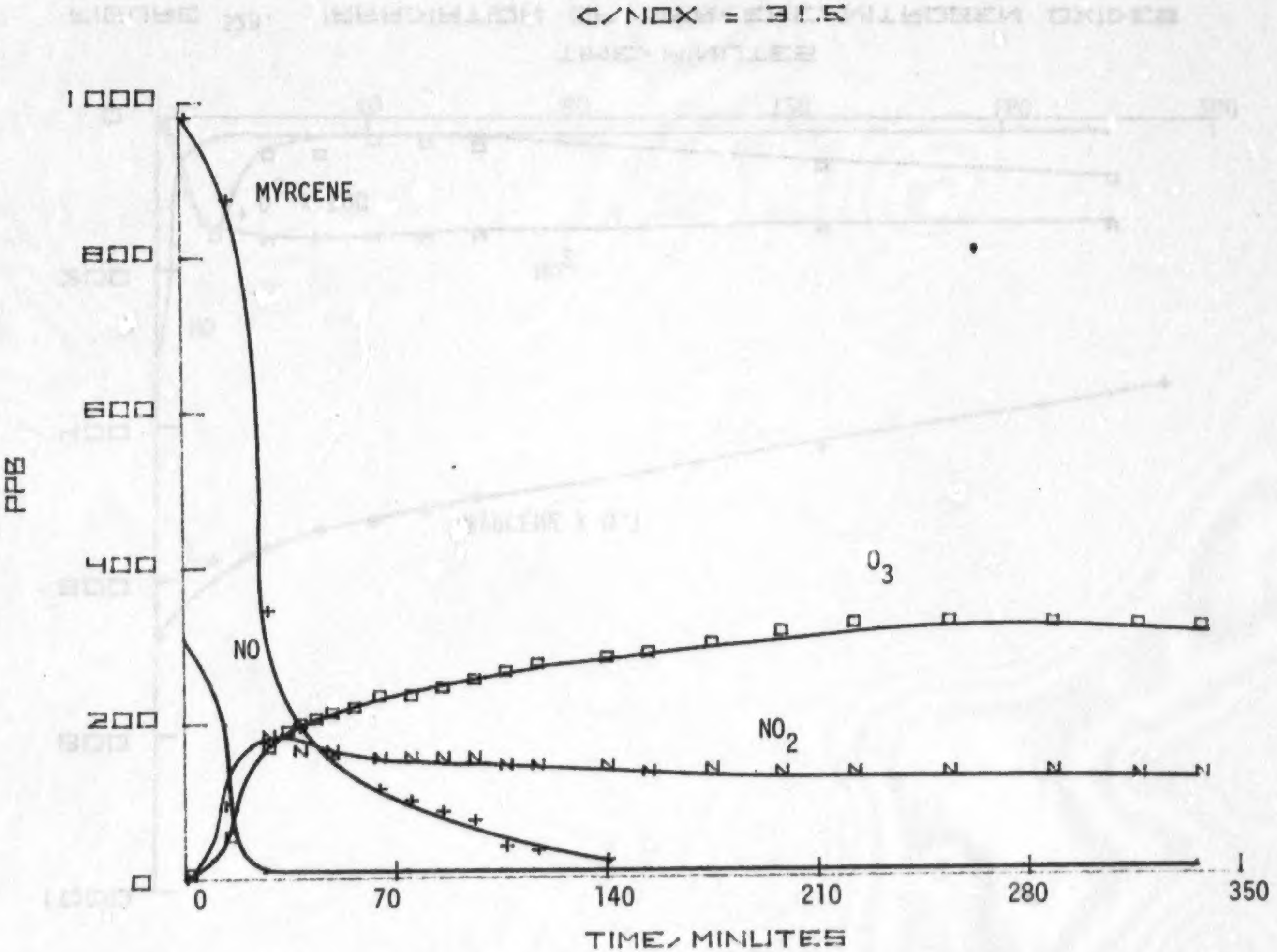


FIGURE 51B. IRRADIATION OF MYRCENE/NITROGEN OXIDES

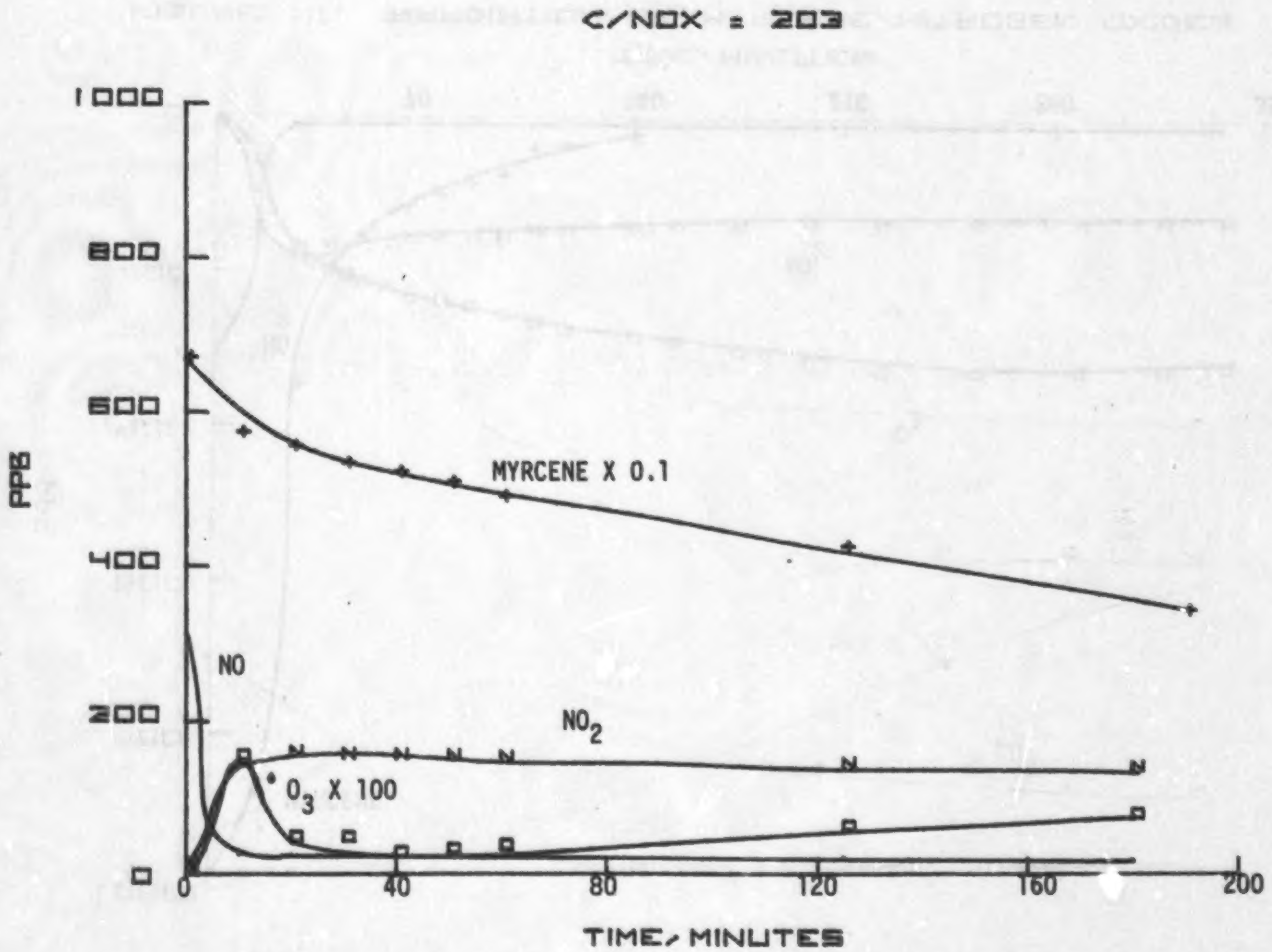


FIGURE 52B. IRRADIATION OF MYRCENE/NITROGEN OXIDES

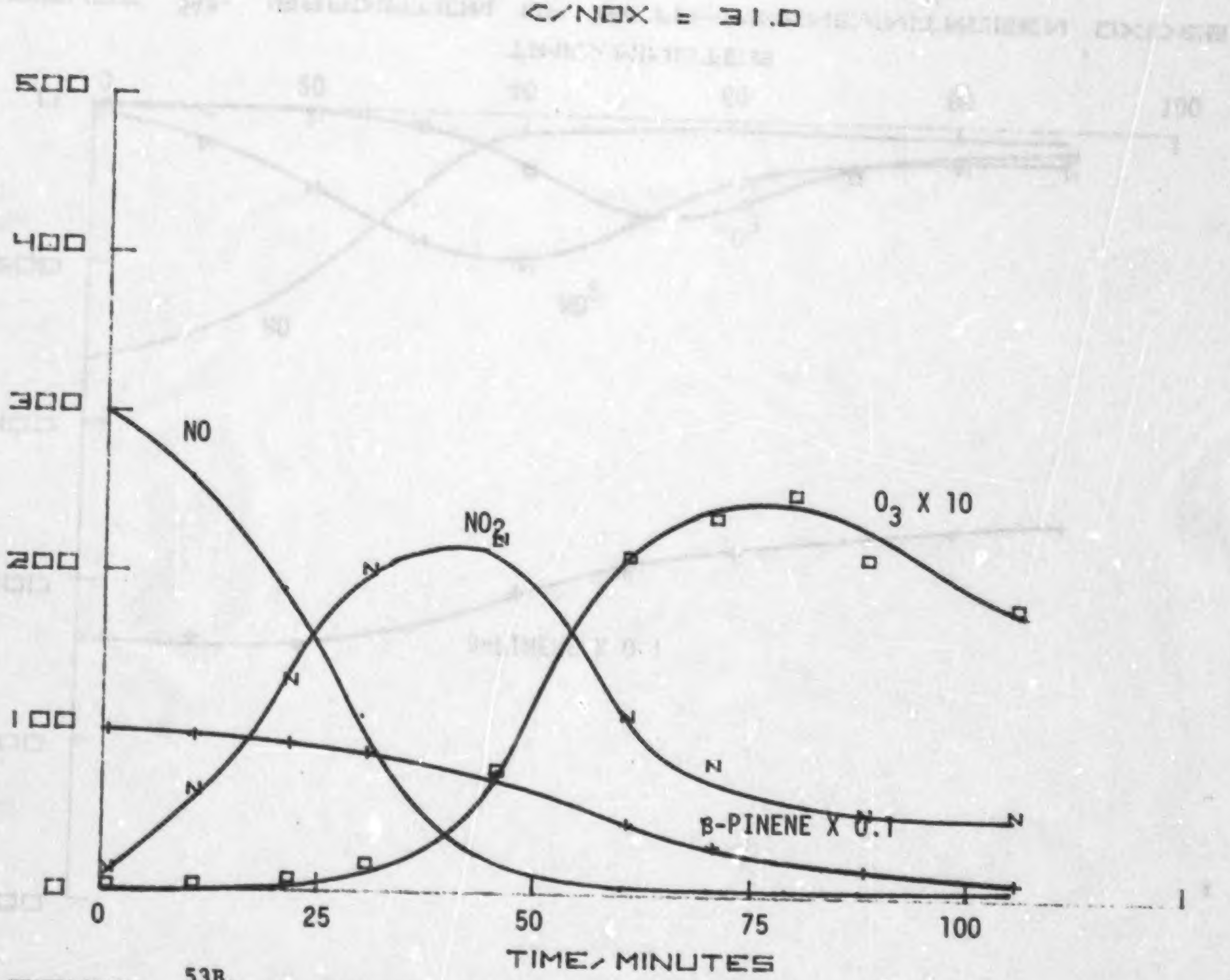


FIGURE 53B. IRRADIATION OF BETA-PINENE/NITROGEN OXIDES

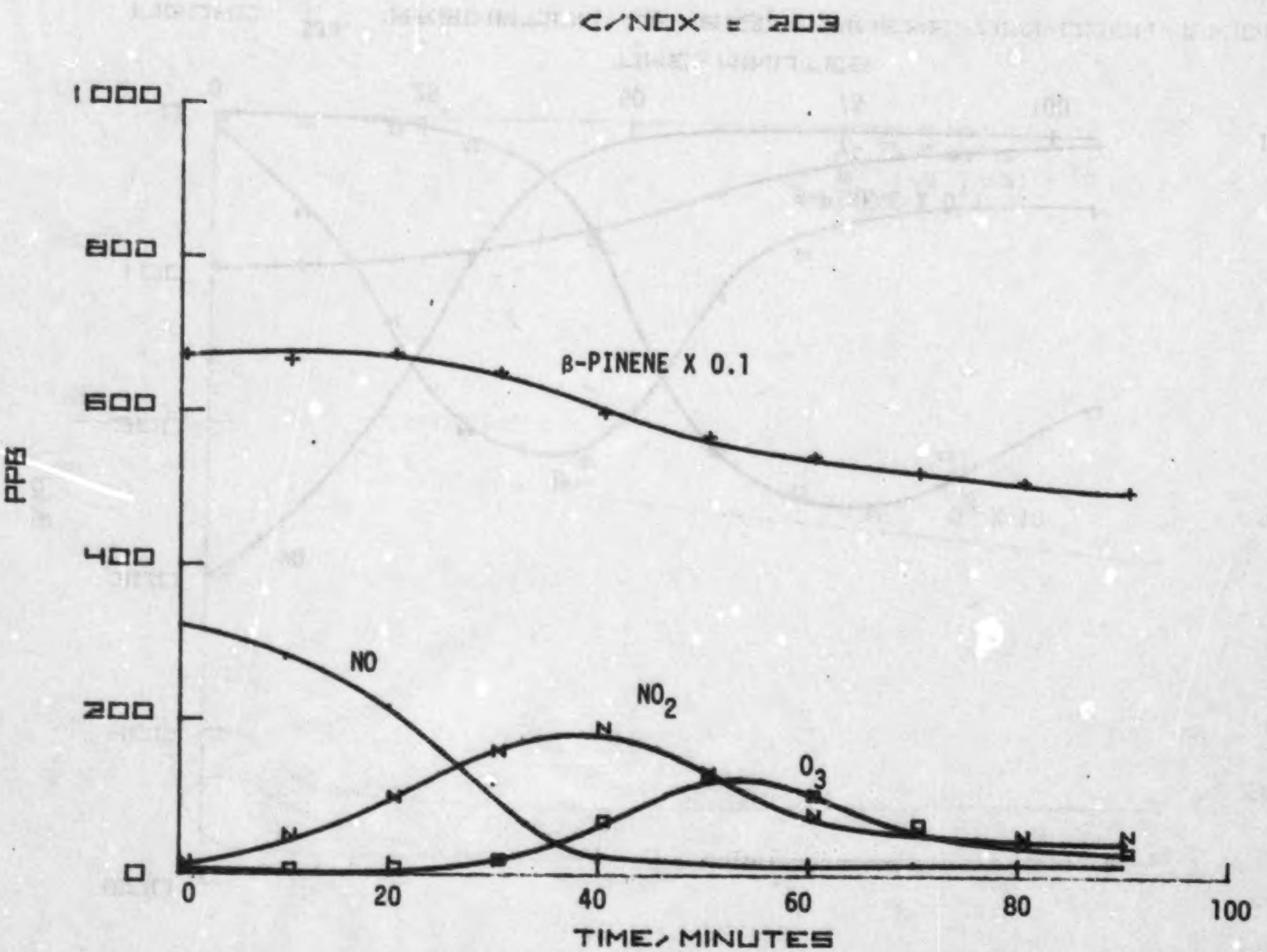


FIGURE 54B. IRRADIATION OF BETA-PINENE/NITROGEN OXIDES

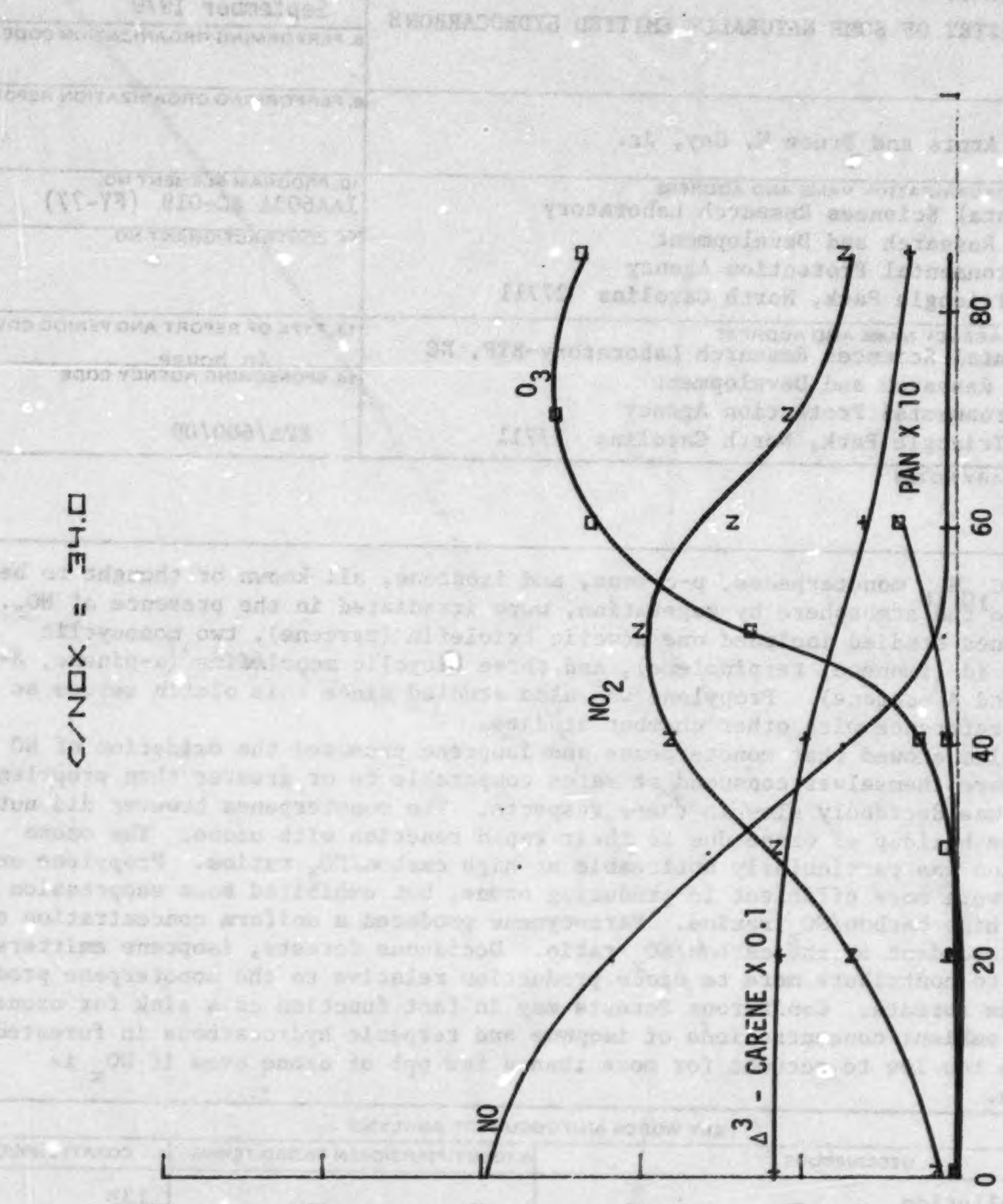


FIGURE 55B IRRADIATION OF DELTA-3-CARENE/NITROGEN OXIDES